



ETHYL ALCOHOL

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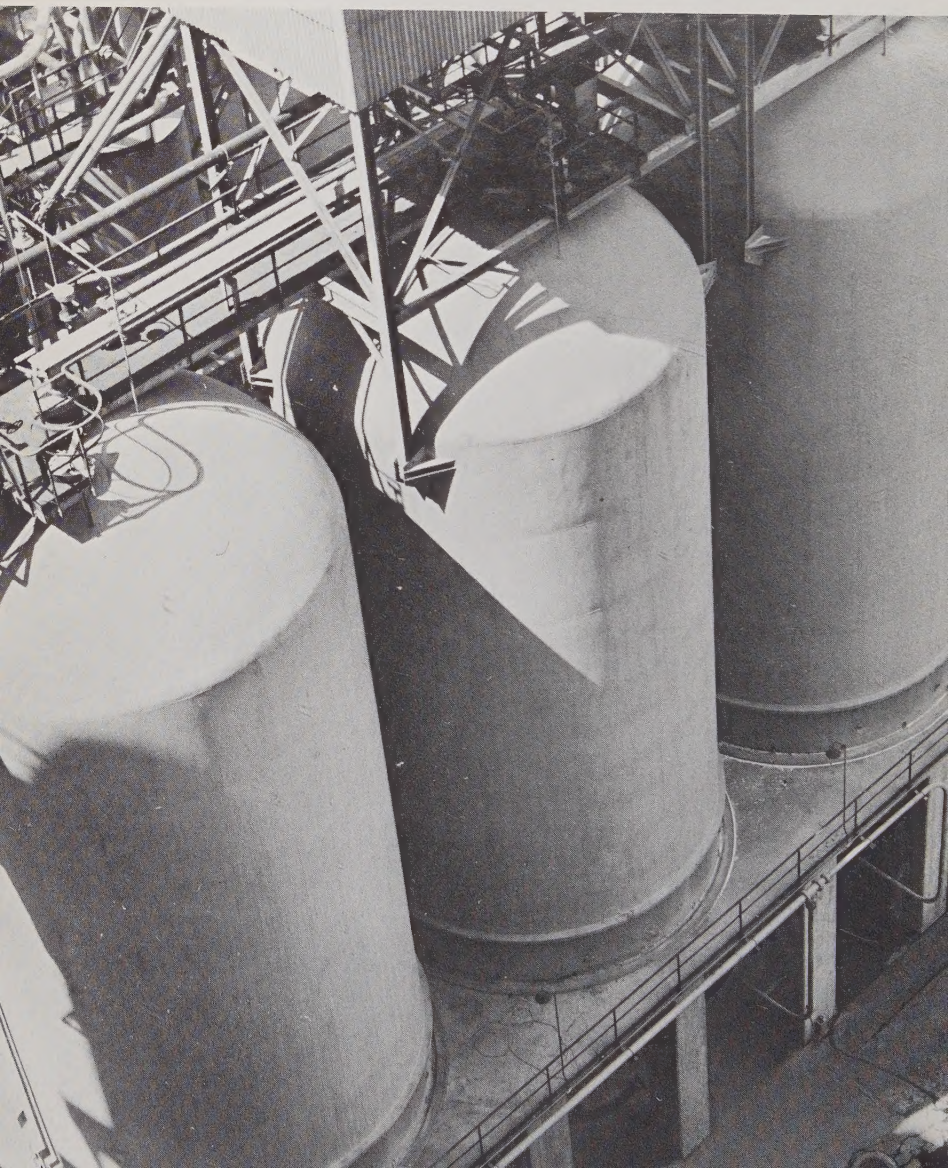


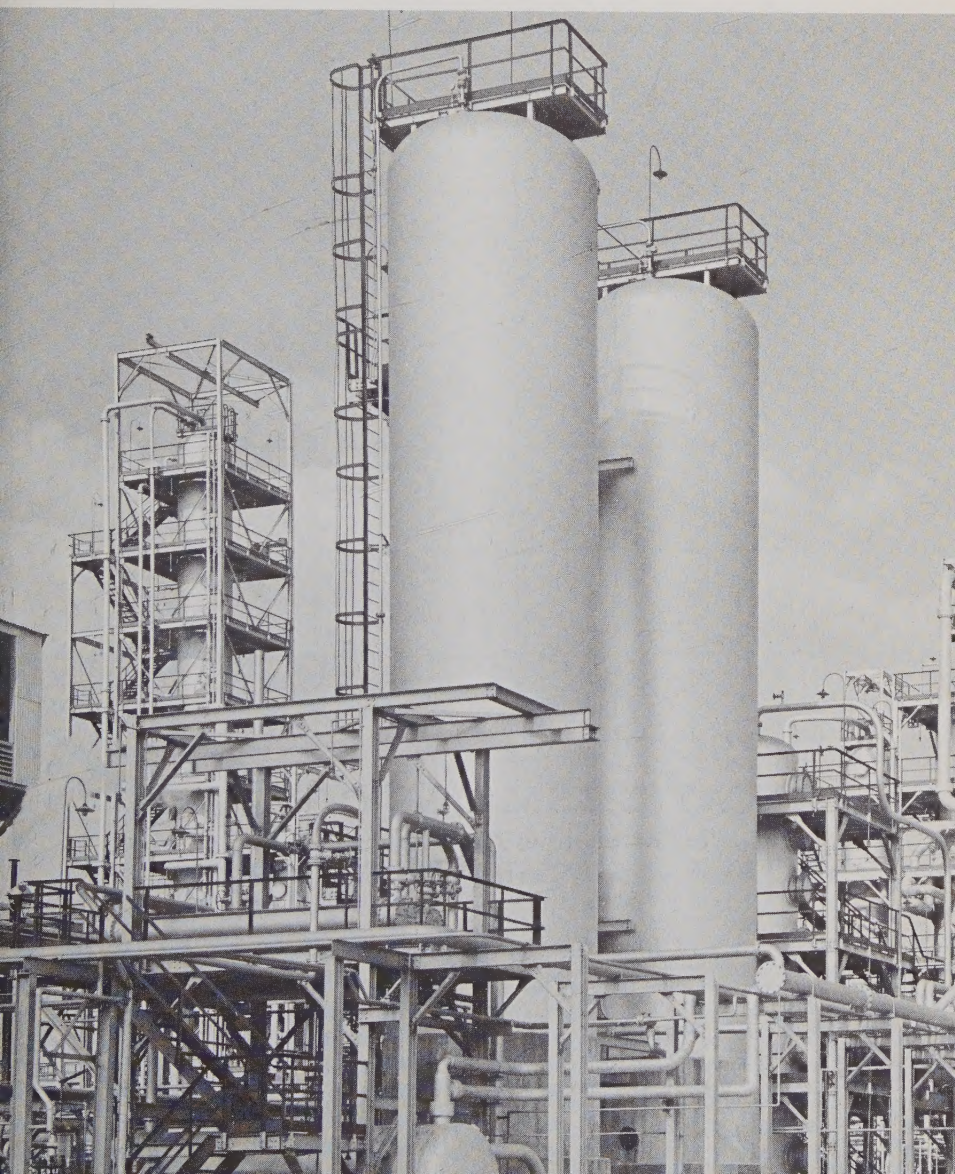
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ETHYL ALCOHOL

Hatch, Lewis F

ETHYL ALCOHOL





ENJAY CHEMICAL COMPANY

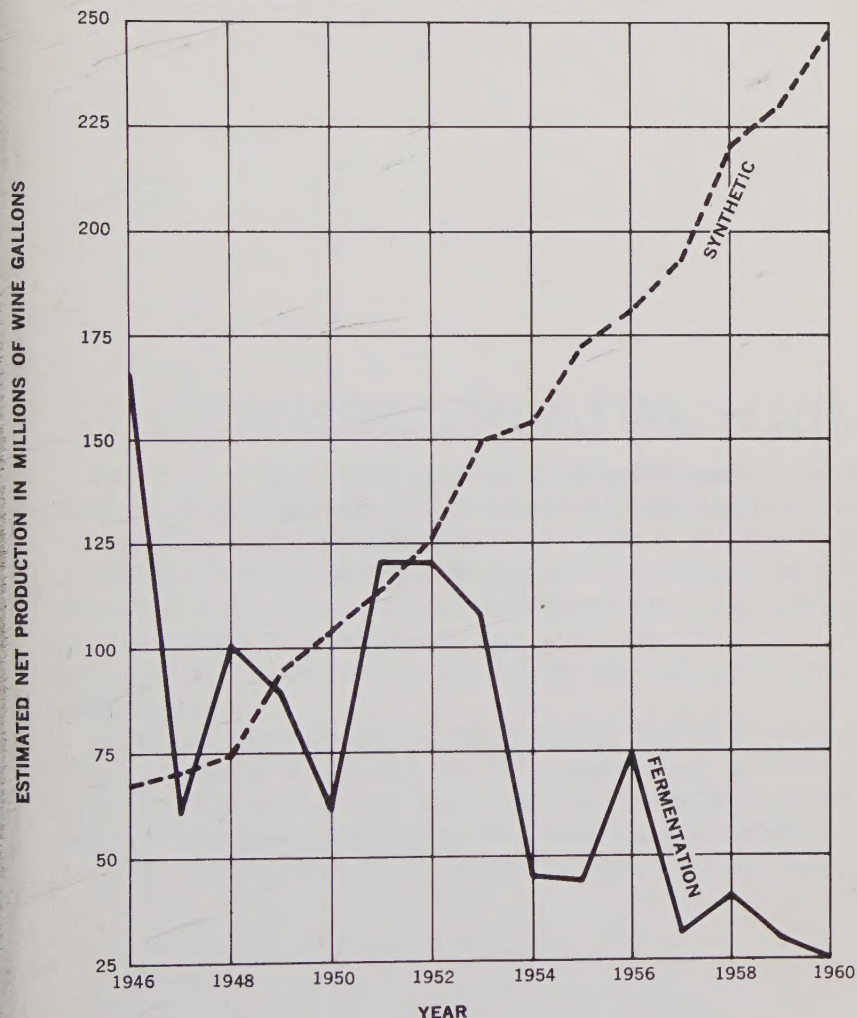
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INDUSTRIAL ETHYL ALCOHOL PRODUCTION



Based on data of the Internal Revenue Service, U. S. Treasury Department for fiscal years ending June 30th. Fermentation production for 1952-1960 includes some beverage alcohol.

This chart illustrates the growth of synthetic ethyl alcohol to its current dominance over fermentation alcohol in the industrial market.

ACKNOWLEDGMENT

This book was written by Dr. Lewis F. Hatch, Technical Consultant, Enjay Laboratories. Several chapters were revised and expanded by Marvin B. Silverberg, Technical Literature Consultant, who reviewed the manuscript prior to publication.

FOREWORD

This book is the third in a series on Enjay Chemical Company products—*Higher Oxo Alcohols* was published in 1957 and *Isopropyl Alcohol* was published in 1961.

Information and data in this book came from technical literature, patents and the Enjay Laboratories. Every effort has been made to report these facts objectively and accurately. It is hoped that this book will be of material aid to users and prospective users of ethyl alcohol.

Enjay has also published an Ethyl Alcohol Handbook which provides additional information on the compositions, specifications, properties and uses of pure and denatured alcohol. A summary of pertinent government regulations also is included. This useful booklet may be obtained through any Enjay Chemical Company office.

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INTRODUCTION

Ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) is a compound of many names and innumerable uses. Its other names, some obsolete but some still used, are ethanol, methyl carbinol, grain alcohol, Cologne spirits, hydrated oxide of ethyl, spirits of wine and aqua vitae. The importance of ethyl alcohol is indicated by the fact that when one speaks of "alcohol," one invariably is referring to ethyl alcohol and not to the class of compounds or to any other individual alcohol.

The name alcohol was originally a generic name for a volatile liquid and was derived from two Arabic words, *al* and *kohl*, which described a finely ground powder used by Oriental women to darken their eyebrows. The name was gradually restricted to ethyl alcohol, "spirits of wine rectified to the highest degree."

The current annual United States production of industrial ethyl alcohol is nearly two billion pounds and hardly an industry or consumer product is without contact with it. It has been said that if the manufacture of ethyl alcohol were to cease suddenly, mankind would be deprived of most of the essentials that safeguard life and contribute to comfort and convenience.

This important chemical raw material and solvent is a volatile, flammable, colorless liquid of mild, characteristic odor. It is generally used as a mixture of 95% by volume of alcohol and 5% water, although anhydrous alcohol is also commercially important. Industrial ethyl alcohol may be purchased as specially denatured alcohol, as proprietary or special industrial solvents, as completely denatured alcohol, and as tax-paid or tax-free pure alcohol. Well over 95% of the industrial alcohol produced, however, is sold as specially denatured alcohol.

Regulations governing the use of ethyl alcohol are issued by the Alcohol and Tobacco Tax Division, Internal Revenue Service, U. S. Treasury Department. These regulations are intended to prevent the use of tax-free industrial alcohol for beverage purposes, with a consequent loss of revenue to the Federal government.

HISTORY

The production of ethyl alcohol by fermentation of carbohydrate-containing materials has been known since antiquity. Even today, Australian aborigines who do not know the relationship between father and child know how to make alcoholic beverage by fermentation. Beverages containing ethyl alcohol were made by the Egyptians more than 4000 years ago and the art of distilling ethyl alcohol has been traced to the Pharaohs (800-700 B. C.) (1, 2).

The first written evidence of the separation of alcohol from fermentation products by distillation is contained in the writings of Master Salernus (d. 1167). By 1500 the art had acquired considerable importance and the first comprehensive book on the subject was published in that year (3). Lowitz (1796) appears to have been the first to prepare approximately anhydrous ethyl alcohol (4). The alcohol was dried by the addition of anhydrous potassium carbonate. It was not, however, until 1808 that the constitution of ethyl alcohol was determined and its relationship to ethane demonstrated. The continuous still was patented by Aeneas Coffey in 1832 and for the first time industrial alcohol was available in quantity. The use of benzene as an entraining agent in the dehydration of ethyl alcohol was studied by Young and Fortey (5) and a patent was issued in 1903 for the commercial development of the process (6).

The first preparation of ethyl alcohol by fermentation is lost in the haze of history; the first preparation of ethyl alcohol from ethylene is shrouded in controversy (7). In 1825 Faraday reported the condensation and combination of olefiant gas (ethylene) with sulfuric acid (8). The product of this reaction was given to Hennell who made the potassium salt which was similar to the salt he had obtained previously by neutralization of the reaction product of fermentation ethyl alcohol and sulfuric acid (9, 10). From these data he assumed that ethyl alcohol would result from the union of olefiant gas (ethylene) and sulfuric acid followed by treatment with water. These observations were generally ignored and in 1835 Liebig (11, 12) categorically denied that ethylene would dissolve in sulfuric acid to the extent noted by Faraday.

The first paper devoted entirely to the synthesis of ethyl alcohol from ethylene was published in 1855 by Berthelot (13). This was a definitive article on the reaction. He also extended the reaction to include the hydration of propylene to isopropyl alcohol (mistakenly identified as *n*-propyl alcohol). Berthelot made no reference to the observations of Hennell and claimed the distinction of being the first to synthesize ethyl alcohol from ethylene. Hennell failed to receive his just recognition until 1895 (14). Berthelot's defense was published in 1899 (15) and Hennell was once more championed in 1902 (16). Herstein has put the controversy in its proper perspective (7): "Hennell clearly indicated the possibility of preparing ethyl alcohol from ethylene by hydration via ethyl sulphuric acid and supported it by partial proof, the credit for complete proof and the extension of this reaction to olefins generally belongs to Berthelot..."

The first patent on this process was by Cottele in 1861 (17). The ethyl alcohol was prepared by passing illuminating gas, which had been dried and freed of hydrogen sulfide and ammonia, into concentrated sulfuric acid. The reaction product was then diluted to liberate the alcohol. In 1862 a liter of ethyl alcohol, said to have been made from the ethylene of coal gas, was shown at the London Exhibition of that year (18). The first Russian literature reference appears to be that of Goryainov in 1873 (19). The industrialization of the production of ethyl alcohol from ethylene in the United States came in 1929-1930. In 1943 Standard Oil of New Jersey became the first oil company to produce ethyl alcohol from petroleum refinery gases. The direct catalytic hydration of ethylene to ethyl alcohol became commercial in 1948. The impact of synthetic ethyl alcohol (ethanol) is indicated by the percentage of industrial alcohol produced from ethylene: 1935, 10%; 1948, 38%; 1952, 57%; 1956, 72%; and 1960, 91%.

The ratio between synthetic and fermentation industrial alcohol now varies from year to year, depending upon different economic factors. The most important factor is the cost and availability of molasses. The wide fluctuations in price and supply of industrial alcohol noted during the early 1950s were caused by similar variations in the price and availability of molasses from Cuba. The current dominance of synthetic alcohol over fermentation alcohol has led to increased price stability in the alcohol industry.

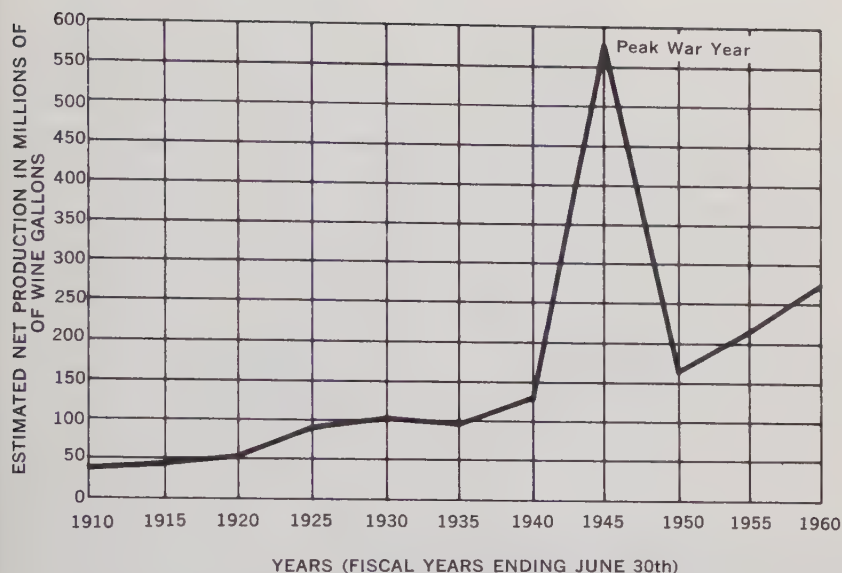


Figure 1. Industrial ethyl alcohol production, based on data of the Internal Revenue Service, U. S. Treasury Department. Production for 1952 onward includes a small amount of alcohol for beverage purposes.

Since 1900 the production of industrial alcohol has varied with fluctuations in business activity but the general trend has been greater than the rate of population growth. The top production of 580 million gallons was attained in the war year of 1945, reflecting the government's program to obtain synthetic butadiene rubber from ethyl alcohol (Figure 1).

The war years of 1941-1945 present a special chapter in the production and use of ethyl alcohol (20). Great demands were made upon the alcohol industry and it wrote a brilliant record of achievement. The end-use pattern for specially denatured ethyl alcohol during a typical war year is depicted in Figure 2. In 1942 all beverage manufacturers capable of producing industrial alcohol were ordered to convert their production. In addition to these facilities, the government built three alcohol-from-grain plants in the Midwest. Other sources of carbohydrate materials were investigated but were not a factor in the overall production picture. These included sawdust

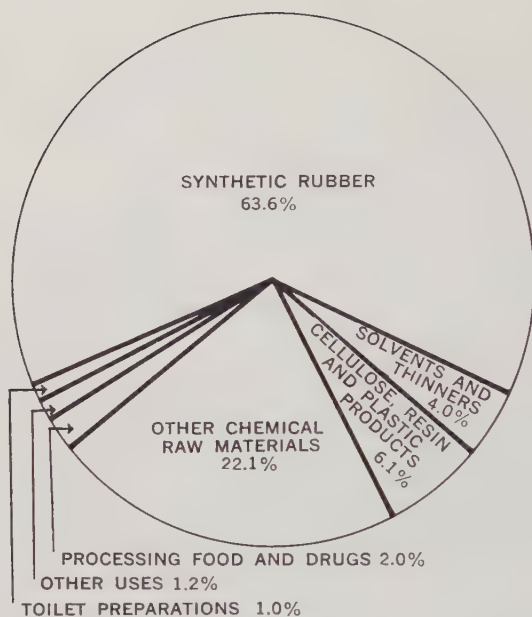


Figure 2. Wartime end-use pattern for specially denatured alcohol, for the year ending June 30th, 1945. (From C. M. Beamer, *Chem. Eng. Prog.*, 43 (3), 92-96, 1947. Copyrighted: reprinted by permission of **Chemical Engineering Progress.**)

and sawmill waste (21, 22), wood waste (23, 24, 25), waste sulfite pulp liquors (26, 27), various farm products (28, 29), and even rejected bananas (30). Synthetic alcohol capacity was increased only slightly because of the wartime scarcities of vital construction materials.

The role of industrial alcohol in our peacetime economy is varied. It is second only to water as a general solvent and it is a key raw material in the manufacture of drugs, plastics, lacquers, polishes, plasticizers and rubber accelerators. The most important area of utilization is in the production of other chemicals. The dehydrogenation of ethyl alcohol to acetaldehyde is the most important from the standpoint of the quantity of alcohol used.

The economics of industrial alcohol presents a very complex picture. The possible raw materials are many. They are related to large and diverse branches of industry and to farm products. The use of ethyl alcohol as a fuel for internal combustion engines has political

and economic implications. The past, present, and future history of ethyl alcohol will make fascinating reading for students in the fields of government, history, sociology, economics, and international relations—as well as chemistry and medicine. Over forty years ago (1920) Tunison made the following prophecy, “May we not look forward to the time when the industry of making industrial alcohol in the United States will be of such a magnitude as to be a great national asset under all conditions?” (31). Truly that time has arrived.

A large number of general and specific articles and other publications have been written about industrial ethyl alcohol. The following references represent a few of these: (1, 7, 20, 31-41).

Definitions

Absolute Alcohol

Pure, anhydrous ethyl alcohol (ethanol). Enjay Chemical Company absolute alcohol is specified to have a purity of 99.9% by volume, minimum.

Apparent Proof

A property of ethyl alcohol solutions containing ingredients other than water, i.e. denatured alcohol. Apparent proof is equivalent to the proof of a pure alcohol-water mixture having the same specific gravity at 60°/60°F as does the solution in question.

Completely Denatured Alcohol (C.D.A.)

Ethyl alcohol to which certain materials prescribed by Federal regulations have been added to make the alcohol unfit for beverage purposes. C.D.A. is tax-free and may be purchased and used within certain limitations without a permit or bond.

Denaturant

A material authorized by Federal regulations to be added to ethyl alcohol to make it unfit for beverage or internal human medicinal use.

Drawback

A tax refund which can be obtained when tax-paid alcohol is used to make certain approved non-beverage products.

Industrial Alcohol

Ethyl alcohol sold and used for non-beverage purposes.

Proof

Twice the percentage by volume of ethyl alcohol in an ethyl alcohol-water mixture at 60°F. For example, 190 proof alcohol contains 95% alcohol by volume.

Proof Gallon

The amount of ethyl alcohol present in one wine gallon of 100 proof alcohol at 60°F. To determine proof gallons, multiply the number of wine gallons at 60°F by the proof and divide by 100. For example, one wine gallon of 190 proof ethyl alcohol contains 1.9 proof gallons.

Proof Spirits

An alcoholic liquid of 100 proof, 50% of whose volume consists of ethyl alcohol having a specific gravity of 0.7939 at 60°F, referred to water at 60°F as unity. One gallon of proof spirits can be made by mixing together 0.5000 gallons of absolute alcohol and 0.5373 gallons of water (shrinkage in volume occurs when the two liquids are mixed). Proof spirits contain 42.49% alcohol by weight and have a specific gravity of 0.93418 at 60°F.

Proprietary Solvent

A solvent containing more than 25% ethyl alcohol by volume, made with specially denatured alcohol according to a formula authorized by Federal regulations. No permit or bond is required to purchase a proprietary solvent. JAYSOL®, Enjay Chemical Company's proprietary solvent, is available in 190 proof and anhydrous grades.

Pure Ethyl Alcohol

Ethyl alcohol which has not been denatured. It is generally available commercially in 190 proof and 200 proof (anhydrous) grades.

Special Industrial Solvent

A solvent made with specially denatured alcohol according to a formula authorized by Federal regulations. Special industrial solvents contain no hydrocarbon denaturants and are restricted to certain industrial and manufacturing uses. No permit or bond is required. JAYSOL-S®, Enjay Chemical Company's special industrial solvent, is available in 190 proof and anhydrous grades.

Specially Denatured Alcohol (S.D.A.)

Ethyl alcohol to which certain materials prescribed by Federal regulations have been added to make the alcohol unfit for beverage purposes. It is tax-free but a Federal permit and bond are required to purchase and use it. S.D.A. can be used in a greater number of Federally specified arts and industries than completely denatured alcohol.

Tax-Free Industrial Alcohol

Pure ethyl alcohol which can be obtained free of tax. Its use is restricted to various governmental agencies, educational organizations, scientific laboratories, hospitals, sanitoriums and non-profit clinics. A permit is required.

Tax-Paid Industrial Alcohol

Pure ethyl alcohol which can be obtained upon payment of the Federal tax of \$10.50 per proof gallon. All or part of this tax will be refunded if the alcohol is used in the manufacture of medicinal or food products unfit for beverage purposes.

Tax Gallon

Equivalent to the proof gallon for spirits of 100 proof or over. For spirits of less than 100 proof, the tax gallon is equivalent to the wine gallon. Since spirits are taxed according to proof, one wine gallon of 190 proof alcohol is taxed as 1.9 proof gallons.

Wine Gallon

A United States gallon of liquid measure (231 cubic inches).

Withdrawal

The act of obtaining ethyl alcohol from a producer, denaturer or bonded dealer in accordance with Federal regulations.



PREPARATION

Industrial ethyl alcohol is produced either synthetically from ethylene or by the fermentation of carbohydrate-containing materials. As shown in Table I, synthetic production (directly from ethylene gas and from ethylene by way of ethyl sulfate) far exceeds production by fermentation.

The most important synthetic process is the esterification-hydrolysis of ethylene, making use of concentrated sulfuric acid. During the fiscal year ending June 30, 1961, 395.6 million proof gallons were produced by this process (about 82% of the total synthetic production). The remainder was produced by the direct vapor-phase catalytic hydration of ethylene. Other methods have been developed for the synthesis of ethyl alcohol but they are not commercial at the present time. One such process involves the esterification of ethylene with dilute acids. Hydration to the alcohol is then carried out in the same equipment. Ethyl alcohol may also be produced by conversion of acetylene to acetaldehyde and hydrogenation of the aldehyde to the alcohol. It is doubtful, however, that this will ever be a commercial process. The Fischer-Tropsch hydrocarbon synthesis produces ethyl alcohol and many other oxygen-containing compounds as by-products and this may become an important source (42).

The three classes of carbohydrates which can be used to produce ethyl alcohol by fermentation are: (1) sugar-containing materials (molasses, sugar beets, sugar cane, sorgo); (2) starchy materials (grains, potatoes); and (3) cellulose and waste products from cellulose processing (wood, agricultural residues and sulfite liquor). The first class can be fermented by yeast without previous treatment. The starchy materials must first be converted to fermentable sugars by enzymatic action or by use of molds or mineral acids. Cellulosic materials are converted to fermentable sugars by the action of mineral acid. Molasses is currently the only important source of fermentation industrial alcohol. Before World War II, most industrial alcohol came from this source while most beverage alcohol came from grains.

The amount of industrial alcohol coming from fermentation has declined steadily during the past few years (see page vii). The

Table I INDUSTRIAL ETHYL ALCOHOL — Production by Type of Raw Material¹

(Thousands of proof gallons of alcohol and spirits of 190 or more proof. Fiscal years ending June 30)

Raw Material	1961	1960	1959	1958	1951	1947
Ethyl sulfate	395,611	390,588	362,151	357,687	184,439	133,306
Molasses	19,967	30,668	39,467	56,676	103,350	54,159
Ethylene gas	86,484	80,612	75,463	61,055	31,324
Products used in redistillation	26,195	13,862	8,393	14,394	35,990	49,546
Grain	85,014	7,949	7,460	7,850	114,609	39,742
Sulfite liquors	6,601	7,574	6,254	5,836	5,594	4,380
Cellulose pulp, chemical, and crude alcohol mixtures	806	2,496	2,057	2,114	1,013	2,422
Fruit	15,233	422	494	610	399	220
Others	970	2,600	1,508	15,146
Total alcohol produced	637,005	534,171	502,712	508,823	481,136	298,881

¹ Figures from earlier years are not directly comparable with those for 1961 because of new tabulating methods. Starting with 1961 some beverage alcohol is included under "grain."

Source: Internal Revenue Service, U. S. Treasury Department.

increase in the ratio of synthetic to fermentation alcohol has been caused by basic economic considerations, which have resulted in the building of new synthetic alcohol plants and the shutting down of fermentation facilities. The available supply of molasses is also a factor. Recent developments in the use of molasses by the mixed-feed industry and the direct on-farm feeding of livestock accounts for much of the molasses once available for fermentation. Moreover, the political relationship with Cuba directly affects molasses availability—in recent years, the supply has been drastically reduced.

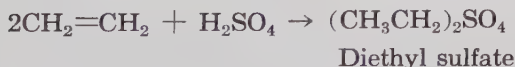
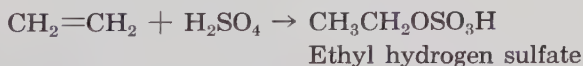
Synthetic Ethyl Alcohol

The production of synthetic ethyl alcohol is based on readily available and comparatively inexpensive ethylene. Ten years ago ethyl alcohol was the most important ethylene consumer but at present it ranks third behind ethylene oxide and polyethylene (Table II). These and other uses assure a stable ethylene supply. The 1960 ethylene requirement of ethyl alcohol was slightly greater than one billion pounds. This ethylene is converted to ethyl alcohol by both the esterification-hydrolysis process (sulfation-hydrolysis process) and by direct catalytic hydration.

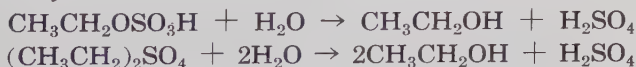
ESTERIFICATION-HYDROLYSIS PROCESS

The preparation of ethyl alcohol by the use of sulfuric acid is a three-step process.

1. *Absorption* of ethylene in concentrated sulfuric acid (esterification or sulfation):



2. *Hydrolysis* of the ethyl sulfates:



3. *Reconcentration* of the dilute sulfuric acid.

The diethyl sulfate may react with ethyl alcohol to form ethyl hydrogen sulfate and ethyl ether (alcoholysis).

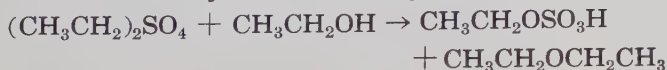


Table II **CONSUMPTION OF ETHYLENE IN PRINCIPAL DERIVATIVES¹**

	Conversion Factor ²	Million Pounds of Ethylene					
		1955	1956	1957	1958	1960 ³	1965 ³
Ethylene oxide	0.9-1.2	1,050	1,130	1,290	1,280	1,510	1,950
Polyethylene	1.05	422	594	744	903	1,230	1,785
Synthetic ethanol	4.4 ⁴	792	845	871	990	1,050	1,200
Styrene	0.33	335	388	389	400 ⁵	452 ⁵	570 ⁵
Halogenated ethylene	0.2-0.5	420	510	545	570	645	760
Others ⁶		31	53	61	72	113	235
Totals		3,050	3,520	3,900	4,215	5,000	6,500

¹ From Chemical Week, May 9, 1959, page 83.

² Pounds of ethylene per pound of product.

³ Estimated.

⁴ 4.4 lb ethylene/gallon 95% alcohol.

⁵ Allowance made for nonethylene-derived styrene.

⁶ Including oxo alcohols and aldehydes, straight-chain higher alcohols, triethyl aluminum, storage, etc.

Ether formation always occurs but it can be reduced to a low figure (ca. 5%) by operating under conditions disadvantageous to diethyl sulfate production. Formation of diethyl sulfate is promoted by high ethylene to acid ratio in the ethylene extract which in turn is promoted by increased ethylene pressure, by increased ethylene concentration and by increased acid concentration. The diethyl sulfate not only causes an increase in ether formation but it is also more difficult to hydrolyze to the alcohol than ethyl hydrogen sulfate.

The ethyl hydrogen sulfate is hydrolyzed by dilution with water. The extent of dilution is controlled by two factors. First, the dilution must be sufficient to prevent the dehydration of the ethyl alcohol to ethylene when the reaction mixture is heated. Second, the dilution is limited by the economics of reconcentrating the dilute acid for reuse. Ethyl alcohol is steam stripped from the dilute acid solution and then concentrated to its azeotropic composition.

The actual operating conditions will vary from plant to plant. The sulfuric acid concentration range is usually between 90% and 98% and the absorption temperature range between 55° and 80°C. The reaction mixture is diluted in a hydrolyzer to give a 50% sulfuric acid effluent when the ethyl alcohol is steam stripped from the acid. The over-all yield is about 90% ethyl alcohol and 5 to 10% ethyl ether. Figure 3 represents a generalized flow diagram for a typical esterification-hydrolysis process.

Guturiya and Dalin have reviewed the literature and patents up to 1935 on the absorption of ethylene by sulfuric acid and have described research then in progress in their laboratories (43, 44). A non-critical review with a comprehensive list of references has been given by Pokrovskii (45) for the journal literature through 1940. The first plant for the production of ethyl alcohol from petroleum ethylene (1943) has been described with a flow sheet and photographs (46, 47). Chemical engineering and design data have been given by Aries in several articles (48). Margolin has presented data on the consumption of ethylene, fuel, electric power, sulfuric acid and steam for the hydration of ethylene by the esterification-hydrolysis process (49). He has also written a review of the production of alcohol from ethylene with special emphasis on Russian experimental work (50).

Many patents have been issued for specific improvements on the

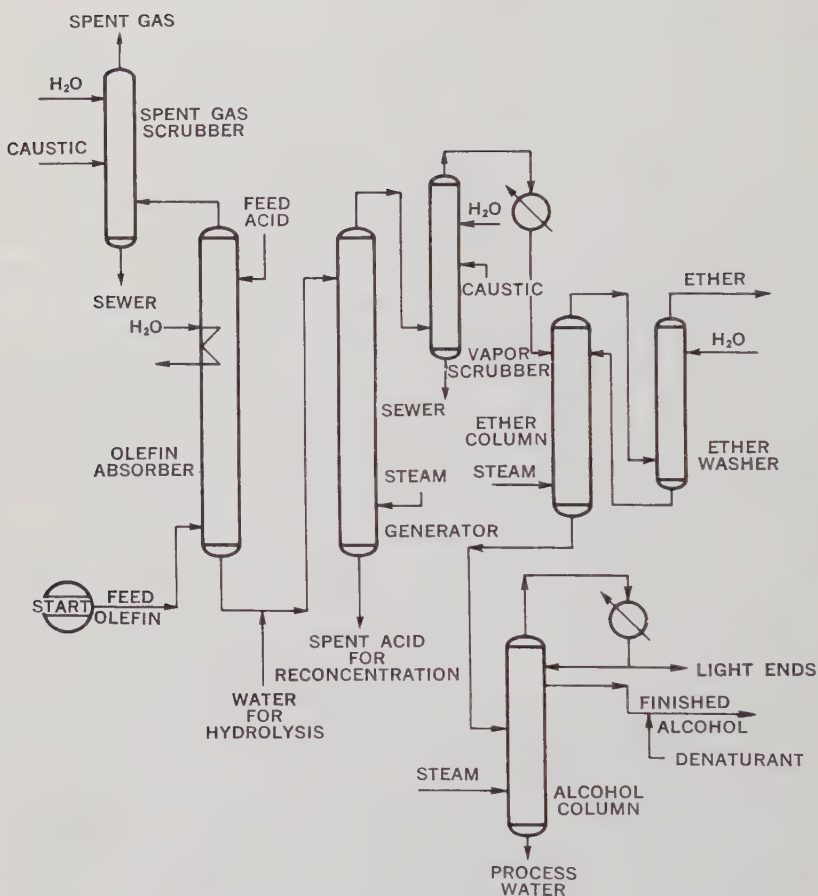
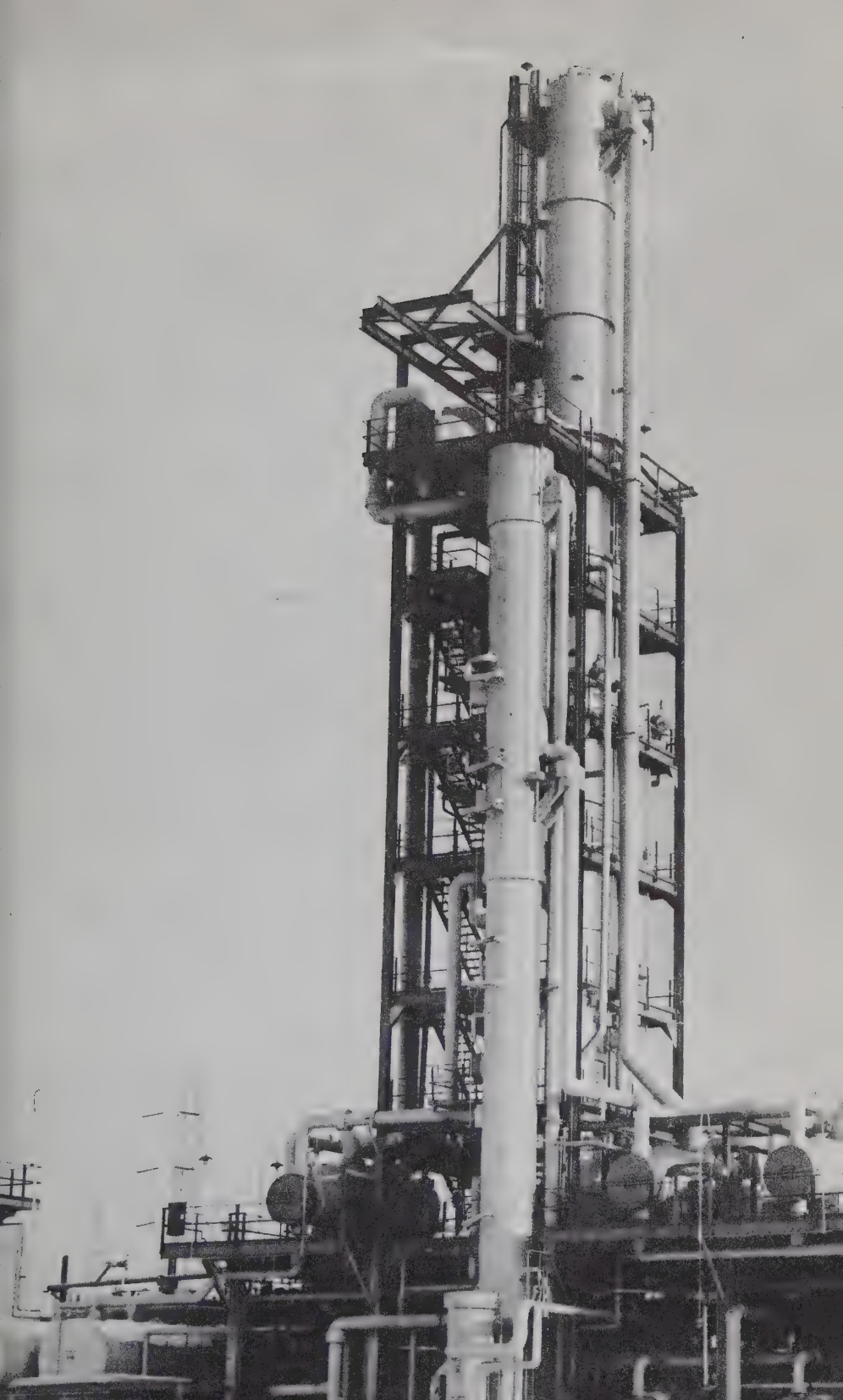


Figure 3. Production of ethyl alcohol by the esterification-hydrolysis process.

process. Some of these will be noted in the section on process variables. The following are typical of general process patents: (51-56).

Feed Materials

Ethylene purity is not a special problem provided that other olefins and diolefins are absent; they are more reactive than ethylene and will polymerize under the sulfation conditions used. Gutuiriya, Dalin and Shenderova studied the effects of propylene in the ethylene feed and report that 0.2% propylene has no effect (94% acid, 65°-70°C, 10-12 atms) but under the same conditions 3% propylene gave 8%



polymers and 35% isopropyl alcohol (57). With 2% propylene and 99% acid the product contained 22.5% polymers and 5.6% isopropyl alcohol. Apparently even small amounts of propylene are detrimental. Butadiene and other diolefins are even more sensitive to concentrated sulfuric acid. Gases containing ethylene intended for the production of ethyl alcohol may be freed from propylene and other higher olefins by treatment at elevated temperatures in the vapor phase with a metallic phosphate catalyst (58). Any remaining higher olefins can be removed by washing with kerosene or with an ammoniacal cuprous salt.

Early attempts to commercialize the process were based on the use of coke ovens or coal gas as the source of ethylene (59). Laboratory scale operations with coke oven gas were reported by Fritzsche (60) in 1898. He noted that pressure and higher temperatures accelerated the reaction but he concluded that large scale production was not yet feasible. The ethylene in coke oven gases (especially those gases produced during the early stages of the operation) was sulfated by de Lattre (1914) (61). It was necessary to remove the hydrogen sulfide, tar and aromatics from these gases before the sulfation. He used vanadium and uranium oxides as catalysts for the sulfation step.

Industrialization of the general process was held in abeyance during World War I but by 1919 the patent literature began to reflect an increase in activity. Most of the patents are related to improvements in the purification of the coke oven and coal gases or to the mechanics of the process. The Skinningrove Iron Company process (62-64), which was developed by Burg and Ollander, was widely publicized by the inventors (65) and others (66, 67). The feed contained 2.0-2.5% olefins (chiefly ethylene) and tar, ammonia, naphthalene, benzene, hydrogen sulfide, and higher olefins which were removed from the gas prior to counter-current absorption in 95 to 97% sulfuric acid between 60° and 80°C. It was estimated that 5800 tons of coal should yield 9280 gallons of absolute alcohol with a 50% conversion of the ethylene. The claims of the patent (62), however, are limited to certain heat exchange principles.

Numerous patents and articles on the preparation of ethyl alcohol from coke and coal gas appeared during the next ten years. The following are representative: for coke oven gas (68-71) and for coal gas (72, 73). A number of others report the use of catalysts with

this type of feed and are noted under the section discussing catalysis of the absorption of ethylene in concentrated sulfuric acid.

It is reported that ethyl alcohol of high purity can be produced from cracked gases containing higher olefins by a combined process in which the higher olefins are alkylated with added isoparaffins through the action of concentrated sulfuric acid (95-100%) (74, 75). The acid layer containing the ethyl ester is separated and hydrolyzed to ethyl alcohol. Hydrofluoric acid (99%) can be used in the alkylation step. A two or more stage process can also be used (76-78). In a two-stage operation (76) the ethylene-containing gases are brought in contact with 87% sulfuric acid in the second absorption zone. The acid from this zone is concentrated by partial dehydration to about 93% and then used in the first absorption zone. Gluud and Schneider have produced ethyl alcohol from coke oven gas which contained 70% ethylene, 20% methane and 10% higher hydrocarbons. The gas was passed through a preliminary concentrated sulfuric acid bath and then, after removal of sulfur dioxide, through absorption towers containing 80% sulfuric acid with 1% by volume of silver sulfate as a catalyst (79).

The ethylene feed stock currently used contains 35% to 95% ethylene with the remaining gases being saturated hydrocarbons (methane, ethane). Based on 1958 figures, approximately 50% of the ethylene produced in the United States comes from natural gas. Refinery gas is the source of approximately 45% of the ethylene produced, while 5% of production originates from other sources, chiefly liquid hydrocarbons. Total ethylene production, 4.2 billion pounds in 1958, is expected to rise to an estimated 6.5 billion pounds by 1965. At that time, natural gas and refinery gas will probably supply 47% each, with 6% coming from other sources (80).

Absorption

The rate of absorption of ethylene by concentrated sulfuric acid may be controlled by such variables as reactor design, acid concentration, ethylene concentration, temperature, pressure, ethyl hydrogen sulfate concentration and the presence of various metal salts. Cambron disclaims that the absorption rate represents the rate of reaction between the ethylene and the acid (81). He suggests that two processes are involved. The first is the solution of the ethylene in the sulfuric acid; the second is the reaction of the dissolved ethylene

with the acid to give ethyl sulfates. Under normal conditions of operation, solution is the slower of the two processes.

The absorption may be carried out industrially by passing ethylene counter-currently through sulfuric acid (95%) in a tower reactor at 80°C under 12 to 30 atms pressure (82). The temperature in the reactor may be regulated within the absorption zone from 65° to 82°C in the upper portion and from about 90° to 110°C in the lower portion (83). This type of operation permits a rapid build-up of the extract to high saturation.

The absorption of ethylene in sulfuric acid is more rapid when the acid contains ethyl hydrogen sulfate (71, 84-86). This has been explained by the greater solubility of ethylene in ethyl hydrogen sulfate than in sulfuric acid (86).

Catalysts are not necessary for efficient absorption but the addition of various materials to the sulfuric acid to increase the rate of absorption of the ethylene has been proposed. A large number of inorganic catalysts are discussed in the literature (61, 70, 78, 79, 87-94) and in many patents. The patent literature to 1937 is reviewed by Ellis (95, 96).

Absorption of ethylene by sulfuric acid is a surface reaction and is inhibited by benzene, *m*-xylene, naphthalene, phenol, aniline, pyridine, quinoline, acetamide, acetone, water and ammonium sulfate (97). The effects of pyridine, water and sulfur trioxide show no discontinuities and the surface tensions of sulfuric acid solutions of these compounds are consistent with the view that inhibition takes place in the surface layer of the liquid. Ethyl ether and nitrobenzene inhibit the absorption of ethylene in sulfuric acid and they, also, lower the surface tension of the sulfuric acid (98). The percentage of inhibition by ethyl ether was directly proportional to the mole percentage of ether in the surface layer as computed by Gibbs' equation. Each mole of ether in the surface seemed to have the power to prevent about five sulfuric acid moles from reacting. The inhibitory action of nitrobenzene was thought to be by another mechanism. It was assumed that a complex of ethylene and sulfuric acid was formed at the surface and was decomposed by the nitrobenzene. Thus, while the actions of the two inhibitors were not the same, they were both related to their concentrations in the surface and not to the total concentration. The inhibition of both ethyl ether and nitrobenzene was much less when the surfaces were static.

Operating variables such as acid strength, temperature and pressure have been investigated extensively. Plant and Sidgwick in 1921 reported on their investigation of the effect of varying these conditions upon the rate of absorption of ethylene by concentrated sulfuric acid (86). They also studied the nature of the products and suggested that the absorption took place in three successive stages: (1) solution of ethylene in the acid, (2) reaction of ethylene with the acid to give ethyl hydrogen sulfate and (3) reaction of ethylene with ethyl hydrogen sulfate to give diethyl sulfate. They concluded that ethyl hydrogen sulfate has a distinct autocatalytic effect and that ethylene must combine with ethyl hydrogen sulfate more slowly than with sulfuric acid. The amount of diethyl sulfate present at any degree of absorption is practically independent of the strength of the acid used. The influence of water present with the sulfuric acid is small apart from its retarding action upon the rate of absorption in general. Table III gives data obtained by Plant and Sidgwick showing the effects of temperature (50° and 70°C) and of various acid concentrations on product distribution. They also used higher temperatures but excessive decomposition was encountered and the data were inconclusive.

The formation of polymers is insignificant below 80°C and at concentrations below 96% (18). With higher temperatures and more concentrated acid, secondary reactions, decomposition, carbonization, and formation of sulfur dioxide and tar are noted.

Neumann has reported that ethylene absorption by sulfuric acid is slight below 50°C, but increases rapidly with increasing temperature and reaches a maximum at 130°C (70). At this temperature he noted appreciable decomposition. With 98% acid at 100°C a brownish color is observed and with stronger acid this occurs at lower temperatures. Formation of ethyl hydrogen sulfate occurs best at about 80°C; above 70°C diethyl sulfate is also formed. In general, the amount of ethyl hydrogen sulfate increases with the strength of the acid so long as water is present; 100% acid does not give good results. Addition of contact substances is equivalent to an increase in temperature and favors formation of undesirable by-products. The use of 98% sulfuric acid has been reported to be more economical than 94% acid (99).

The absorption of ethylene is greatly accelerated by the use of pressure and is roughly a linear function of the pressure (18, 90, 100).

Table III

SULFATION OF ETHYLENE

Effect of Temperature and Acid Concentration
on Product Distribution¹

Temperature °C	Acid conc. Wt %	% Increase in Wt of acid	Product Distribution, Wt %			
			Ethyl Hydrogen Sulfate	Diethyl Sulfate	Sulfuric Acid	Water
50	93.1	16.6	60.1	Nil	33.9	6.0
	97.6	29.2	73.9	15.8	8.4	1.9
	99.3	32.0	72.7	22.2	4.6	0.5
70	93.1	20.8	69.5	2.2	22.5	5.8
	95.8	28.0	79.1	9.4	8.2	3.3
	98.1	34.4	74.8	20.3	3.5	1.4
	98.8	36.2	68.1	29.3	1.7	0.9
	100.1	38.6	70.0	30.0	Nil	Nil

¹ Plant, S. G. P. and Sidgwick, N. V., *J. Soc. Chem. Ind.*, 40(2), 14T (1921).

The rate of absorption of the ethylene using 95% acid at 80° to 90°C shows very little falling off until 1.5 moles of ethylene are absorbed per mole of sulfuric acid (18). The use of pressure within the range of 250 to 500 psi is particularly convenient and in addition, this prevents vaporization loss of diethyl sulfate from rich acid reaction mixtures. Simek has shown that increasing the ethylene partial pressure from 10 to 23.5 atms reduced sulfuric acid consumption and shortened the reaction time (101). Increase in pressure has also been reported to lower consumption of sulfuric acid 7-17%, cut acid loss by 4-8% and shorten reaction time 25-30% (99). Strahler and Hachtel investigated the absorption of ethylene by sulfuric acid under pressures up to 20 atms (102).

Large yields of diethyl sulfate are produced by the solution of excess ethylene in the ethyl hydrogen sulfate-acid mixture and its production is readily affected by pressure. Ethylene under 500 psi pressure (98% acid, 80°C) resulted in 1.60 moles of ethylene combined with 1.00 mole of sulfuric acid in 50 minutes, as compared with 1.18 moles under 20 pounds pressure (18). Maimeri used 100%

acid and 98% ethylene to obtain a yield of 35% diethyl sulfate and 51% ethyl hydrogen sulfate (based on the sulfuric acid) at 3.5 atms pressure (103). At 10 atms pressure the yields were 62% and 30% respectively. He also patented a process to obtain diethyl sulfate which consisted of absorbing ethylene in concentrated acid between 65° and 75°C under low pressure and diluting the acid product to precipitate the diethyl sulfate (51). Curme proposed to make diethyl sulfate commercially by using pure ethylene and volatilizing the diethyl sulfate from the acid mixture in a stream of excess gas (55).

The rate of absorption is increased by more efficient contact between the gaseous ethylene and liquid sulfuric acid (67, 70, 90, 91).

The partial pressures of ethylene in 95.4% sulfuric acid from mole fraction 0.1280 to mole fraction 0.3122 have been determined experimentally and the activities for ethylene in the same range of concentrations were calculated (104).

Hydrolysis

The mixed esters (ethyl hydrogen sulfate and diethyl sulfate) formed by the reaction between ethylene and concentrated sulfuric acid are hydrolyzed by a measured volume of water sufficient to give a 50% aqueous sulfuric acid solution after hydrolysis. The hydrolysis mixture containing ethyl alcohol, ethyl ether, sulfuric acid and water is separated in a stripping column to give dilute sulfuric acid bottoms and a gaseous alcohol-ether-water mixture overhead. This mixture is washed with a counter current of water or dilute caustic soda solution to remove traces of acid. The washed gaseous mixture is then condensed and purified by distillation.

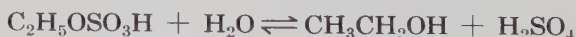
The general process may be modified in various ways and this is reflected by the patent literature. Shiffler and Holm have described a continuous distillation process in which the acid liquor is introduced into the central portion of a reflux column from the lower end of which liquor is continuously withdrawn, passed through a boiler and returned to the lower end of the column (105). Alcohol-free acid is removed from the bottom of the column and alcohol-rich distillate is continuously removed from the upper portion of the column. They also claim the separation of uncondensed gases from the condensed distillate and the extraction of alcohol from the gases by absorption in water and recycling of the water and alcohol mixture to the acid liquor being introduced into the tower. Muller and co-workers have

proposed similar processes (106, 107). The ethyl sulfates may be continuously hydrolyzed by slowly adding them to boiling water at such a rate that at no time is there a high concentration in the hydrolysis mixture of either ethyl sulfates or ethyl alcohol (108). Any diethyl sulfate removed with the alcohol is continuously separated and returned to the hydrolysis mixture. The hydrolysis temperature may be kept at 80° to 90°C by first cooling the strong acid reaction mixture to 30° to 50°C, partially diluting it to 85 to 95% acid strength, cooling it again to 30° to 50°C, and then hydrolyzing the ethyl sulfate by dilution with water to an acid concentration below 60% (109).

Diethyl sulfate is fairly stable in the presence of water at temperatures below 70°C (57). The hydrolysis is promoted by hydrogen ions and it is markedly more rapid in the presence of free sulfuric acid.

Ethyl ether is formed during hydrolysis when the acid reaction product contains diethyl sulfate. The ether is formed by the reaction between the diethyl sulfate and ethyl alcohol (page 13). Thus its formation can be reduced by separating the diethyl sulfate from the reaction product. Diethyl sulfate can be hydrolyzed separately with water or dilute acid, with vigorous agitation, or by adding the ester gradually to boiling water in which the concentration of alcohol is kept low by distilling the alcohol as rapidly as it is formed (108). It has been proposed to reduce ether formation by conducting the hydrolysis in two steps (110). In the first step, the acid absorption mixture is diluted with water to a 40 to 55% acid concentration and a major portion of the diethyl sulfate present is hydrolyzed at 80° to 90°C. The hydrolysis is completed at 80° to 95°C in the second step. In a single step process, separate streams of the diethyl sulfate solution and water are brought together in the hydrolysis zone. A sufficient concentration of ethyl alcohol is maintained to prevent the formation of a separate diethyl sulfate phase (111). A temperature of 80° to 90°C in the hydrolysis zone, a sulfuric acid concentration in the diluted solution of 45% and a time of residence in the zone of 14 to 17 minutes are claimed.

Kremann has investigated the hydrolysis of ethyl hydrogen sulfate



and reports that the equilibrium constant of the reaction is apparently independent of temperature. The velocity of the reaction between

ethyl hydrogen sulfate and water is proportional to the hydrogen ion concentration (112). There is some confusion in the literature regarding the effect of hydrogen and hydroxyl ions on this type of hydrolysis (18). Kremann reported that the hydrolysis of barium ethyl sulfate was retarded by hydrogen ion (113) but Drushel and Linhart clearly showed this to be in error (114).

Several patents have been issued to Compagnie de Béthune for the hydrolysis of ethyl hydrogen sulfate by the reaction with ammonia gas and steam (115, 116), and for the addition of ammonia gas so that the hydrolysis and distillation of the alcohol follow without the application of external heat (117).

The dissociation and decomposition of ethyl hydrogen sulfate at different temperatures has been investigated by Kremann (118). The partial pressures of ethyl alcohol in 62.81% sulfuric acid have been measured and the activities calculated for concentrations up to mole fraction 0.2400 (104).

Acid Reconcentration

The reconcentration of the dilute sulfuric acid (50%) resulting from the hydrolysis of the ethyl sulfates is one of the more costly operations in the production of ethyl alcohol by the esterification-hydrolysis process. A large fraction of the capital investment for this process is centered in the concentration facilities. With one type of concentrator, large quantities of steam are used and with another there may be a fume nuisance. Maintenance costs are high and acid consumption is significant.

Various types of acid-concentrating equipment and processes are in use. In one process the dilute acid is passed through a reboiler where sufficient water is evaporated to raise the acidity to 70%. The 70% acid is concentrated to 90% in a two-stage vacuum evaporator operating at pressures of 2.5 and 0.4 in. Hg absolute, respectively. Dowtherm A is the heating medium and it operates at 20 psi and 300°C. The temperature of the acid is kept below 190°C during its reconcentration.

The buildup of organic material in the sulfuric acid presents one of the serious problems of acid reconcentration. The acid can be reconditioned by heating it at 175-200°C under the vapor pressure of the acid for at least one hour before it is concentrated under vacuum to the desired strength (119). It is reported that oil and tar can be

separated by cooling the dilute acid (120). Suspended carbon may be removed by diluting the acid with a hydrocarbon oil (kerosene) which absorbs the carbon, tar, etc. The oil is subsequently decanted to leave a carbon-free acid (121). Foaming of dilute sulfuric acid during reconcentration is reduced by adding, as an antifoamant, an oxidized alkyl sulfate reaction product formed by the reaction between 82 to 96% sulfuric acid and a C₃ or C₅ aliphatic alcohol, propylene or amylene (122). Foaming may be reduced in sulfuric acid concentrated to at least 90% by heat soaking the acid for one to fifteen hours at 150-280°C under sufficient pressure to prevent boiling (123).

DIRECT HYDRATION OF ETHYLENE

The vapor phase catalytic hydration of ethylene has received appreciable study concerning both the theoretical requirements of the reaction and the many substances which might catalyze the reaction.



The patent literature through 1937 for the use of catalytic amounts of acids and of other types of catalytic materials (as well as the theoretical aspects of the reaction and their practical implications) has been reviewed by Ellis (95, 96). The following references contain additional material related to theoretical problems: (124-128).

At ordinary temperatures only a relatively small amount of ethyl alcohol is present in the vapor phase equilibrium mixture and an increase in temperature decreases this alcohol concentration. The equilibrium may be shifted toward the alcohol, however, by an increase in pressure because of a decrease in the number of molecules (an application of Le Chatelier's principle). The reaction velocity is low at low temperatures; thus, it is necessary to use catalysts and relatively high temperatures for equilibrium to be approached or established within a reasonable time.

Nelson and Courter have described the first successful industrial application of the vapor phase catalytic hydration of ethylene (129). The following operating conditions are given using a phosphoric acid-on-Celite catalyst (130).

Reaction temperature	299°C
Reaction pressure	1000 psig
Reaction feed concentration, water-free basis ...	85%
Ethylene make-up concentration	97%

Water-to-ethylene molal ratio in feed	0.6
Space velocity (Volumes of gas at 60°F and 1 atm/min/vol catalyst)	30
Ethylene conversion per pass	4.2%
Water conversion	7.0%

A process flow diagram of both the hydration section and the purification section of the catalytic vapor phase hydration process is given in Figure 4.

Many catalysts for the direct hydration of ethylene have appeared in the general and the patent literature. This literature is too extensive to permit a complete review in this book but the following general references in addition to those already given will be of value in obtaining an over-all appreciation of the past work in this area. Dalin (1956) has reviewed the catalytic hydration of ethylene in the presence of phosphoric acid supported on tabletted synthetic aluminum silicate and on a silica gel of coarse porosity (131). Other catalysts include tungsten oxide (blue tungsten oxide) (132-134), tungsten oxide plus titanium oxide (135), and tungstic acid on silica (136). The hydration of ethylene on a semi-commercial scale over a silicotungstic acid on silica gel catalyst has been reported by Muller and Waterman (137).

MISCELLANEOUS METHODS OF PREPARATION

In addition to the esterification-hydrolysis process and the direct hydration process, various compounds and other processes have served for the production of ethyl alcohol. None has achieved commercial importance although some have received considerable developmental research. These include the hydration of ethylene by dilute acids, the hydration of ethyl ether, the hydrolysis of several different ethyl esters, the hydrogenation of acetaldehyde, the oxidation of hydrocarbons, and the reaction between carbon monoxide and hydrogen.

Hydration of Ethylene by Dilute Acids

In this process, esterification and hydrolysis are carried out in the same equipment and the acid in effect acts as a catalyst. The process makes use of (1) 50-70% sulfuric acid, (2) 0.5-10% sulfuric acid, or (3) other mineral acids or salts. Acid reconcentration is unnecessary, making it possible to achieve considerable economies. High temperatures and pressures are generally required, however, and special

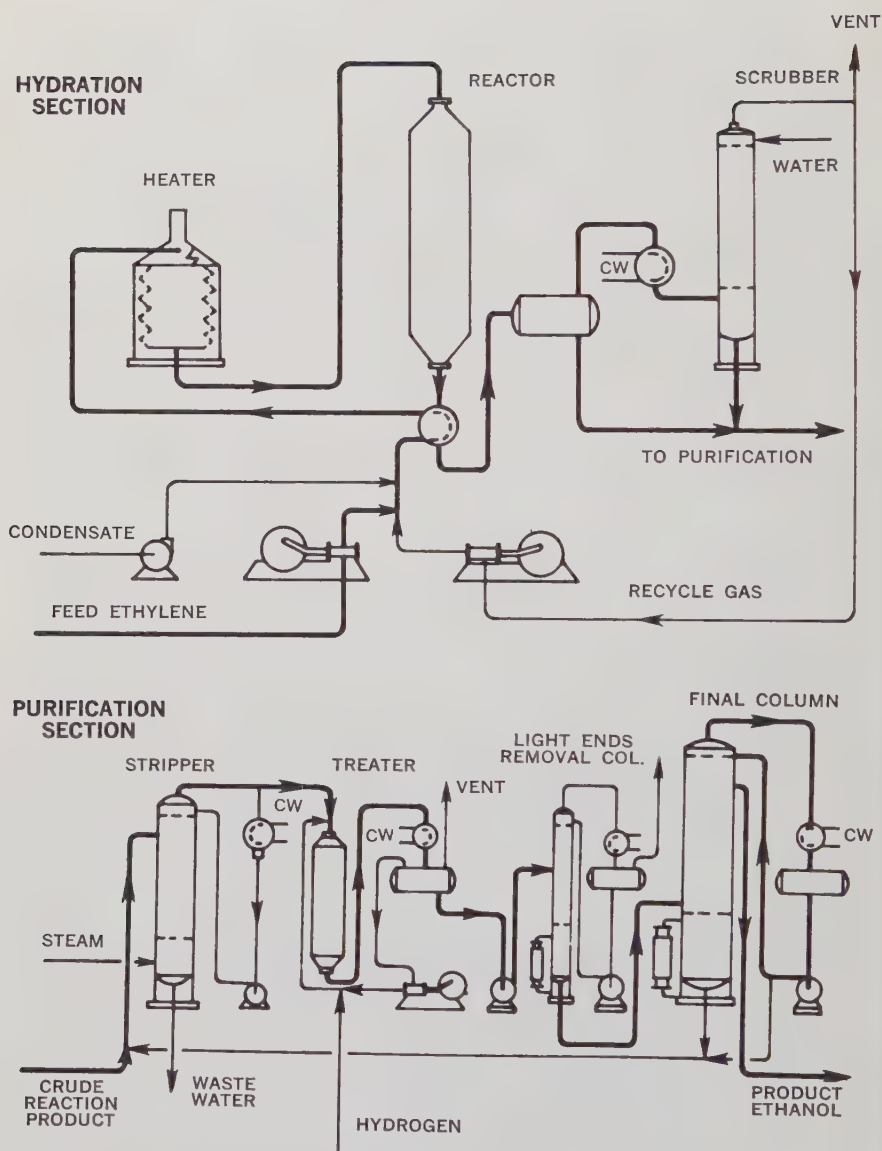


Figure 4. Vapor phase catalytic hydration of ethylene. (From Nelson and Courter, *Chem. Eng. Prog.* 50, 528 (1954). Copyrighted: Reprinted by permission of **Chemical Engineering Progress**.)

equipment must be used to combat the severe corrosion problems encountered.

van Raay in 1958 patented a method for the production of ethyl alcohol by counter-current absorption of ethylene in 68-72% sulfuric acid at 20-40 atms and 140-160°C, with subsequent addition of about 7% water (138). The total yield of alcohol is reported to be over 90%, based on the ethylene. The sulfuric acid leaving the process is at nearly the same concentration as the input acid.

Much research work has been done and a number of other patents have been issued on this process (139-157). Pressures ranging from 50 psi to 3000 psi and temperatures from 100°C to 300°C have been experimented with. A wide variety of catalytic materials have been employed with varying success, i.e.; phosphoric acid, hydrochloric acid, nitric acid, silver sulfate, zinc sulfate, lead sulfate, lithium sulfate, mercuric chloride, silver nitrate, and the sulfuric esters of glycols, polyvalent alcohols or fatty acids.

Ethyl Ether

The hydration of ethyl ether to ethyl alcohol is a reversible reaction catalyzed by acid catalysts and metal oxides.



The acid may be 10% sulfuric acid, 5-6% hydrochloric acid or 15-20% phosphoric acid or salts which hydrolyze to give acid solutions (aluminum chloride, zinc chloride) (158). These are typical; many other concentrations and other acids have been patented. Aluminum oxide has been the most widely studied oxide catalyst (159, 160). Both types of catalysts require a high temperature (ca. 250°C) to be effective. Higher sulfuric acid concentrations permit the use of lower temperatures.

Hydrolysis of Ethyl Esters

A number of esters other than ethyl hydrogen sulfate and diethyl sulfate may be hydrolyzed to ethyl alcohol. None has economic importance, however. The products from the absorption of ethylene by chlorosulfonic acid, followed by hydrolysis of the chlorosulfonic ester, are hydrochloric acid, sulfuric acid and ethyl chloride, in addition to ethyl alcohol (161). The hydrolyses of both diethyl sulfite (162) and ethyl acetate (163) have also been proposed. The hydrolysis of ethyl chloride to ethyl alcohol has received very little industrial attention because of the economics involved.

Hydrogenation of Acetaldehyde

The hydrogenation of acetaldehyde to ethyl alcohol (164, 165) would be an attractive process if it were not for the fact that the most important use for ethyl alcohol is the production of acetaldehyde by the dehydrogenation of ethyl alcohol.

Oxidation of Hydrocarbons

Hydrocarbons may be oxidized to yield a variety of oxygen-containing compounds including ethyl alcohol. A 51% yield of ethyl alcohol has been obtained by the slow combustion of ethane (166, 167). The oxidation of propane has been reported to give an 8% yield of ethyl alcohol (168). Frolich has studied the oxidation of various hydrocarbons to alcohols, acids, aldehydes and other products between 350-700°C and 70-250 atms (168-170).

Carbon Monoxide and Hydrogen

The Fischer-Tropsch process for the production of motor fuels is based on the reaction between carbon monoxide and hydrogen over promoted iron catalysts. By varying the catalyst and the reaction conditions, a variety of oxygenated chemicals can be produced with ethyl alcohol as the principal one (136, 171-178). Morrell, *et al.* have written a definitive paper on the products of this reaction (179).

A plant at Brownsville, Texas was designed to produce annually *ca.* 2.5 million barrels of synthetic fuel and *ca.* 64 million pounds of ethyl alcohol along with about 80 million pounds of other oxygen compounds. The plant, however, never operated at more than 15% capacity and has now closed (180). The process is technically feasible but, at present, economically unsound as it can not produce gasoline and chemicals from natural gas (the source of the carbon monoxide and hydrogen) as economically as they can be produced by other methods.

Fermentation Ethyl Alcohol

Any material which can be fermented may serve as a source of industrial alcohol. Some of these materials were noted in Chapter 1 in respect to the efforts to produce alcohol during World War II. At one time there was a small production of industrial alcohol by the fermentation of raisins (181) and it has even been proposed that alcohol be recovered from the vapors rising from bakers' ovens (182).

Alcohol production from sugar-containing waste products is relatively costly and accounts for an insignificant portion of the industrial production of ethyl alcohol. Corn, grain sorghum, wheat, rye, barley, and potatoes have been used for industrial alcohol production in times of emergency but normally they command much higher prices as foodstuffs. The U. S. Department of Agriculture has published a bulletin showing approximate yields of alcohol from several farm commodities along with various other information (32). Similar information has been reported by others (183, 184). About one and one-half per cent of the annual production of industrial alcohol comes from farm products (Table I). The production of alcohol from wood (185-187), wood wastes (188), and cellulose (189-194) has been studied extensively in foreign countries but has never achieved lasting success in the United States. Sulfite liquors account for a little over one per cent of the annual United States production of industrial alcohol.

MOLASSES

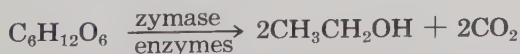
Blackstrap molasses is a by-product of cane sugar mill operations and is a 50% to 60% mixture of sugars. Sucrose is the principal sugar in molasses with the remaining being invert sugar. Invert sugar is the equimolar mixture of glucose (dextrose) and fructose (levulose) formed by the hydrolysis of sucrose.

To start the fermentation process, molasses is diluted to a 14% to 18% sugar concentration and acidified with sulfuric acid to form a mash. Yeast culture is then added to the mash in sufficient quantity to give a 3% to 5% yeast concentration. The yeast contains the enzymes invertase and zymase. Invertase catalyzes the hydrolysis of the sucrose to invert sugar.



The name "invert sugars" is derived from the change in the optical rotation of the sugar solution as a result of this hydrolysis.

The invert sugars are converted to ethyl alcohol and carbon dioxide by the action of the zymase enzymes.



The temperature of the fermentation must be carefully regulated. It may be necessary to add nutrients to the mash to sustain the yeast.

The time required for the fermentation process will range from 36 to 48 hours. The resulting mash is called "beer" and contains between 6% and 12% alcohol. The alcohol is recovered from the mash by steam distillation and the residue is called "slop."

The fermentation of molasses, in common with most natural processes, produces a number of by-products. These include other alcohols, aldehydes, and esters which distill over with the ethyl alcohol and must be removed by redistillation. The principal organic by-product is fusel oil from which amyl alcohol ($C_5H_{11}OH$) is obtained. The carbon dioxide formed during the fermentation process is also a valuable by-product. Its main use is for the production of dry ice.

CONCENTRATION AND PURIFICATION

The concentration and purification of ethyl alcohol produced by fermentation, the esterification-hydrolysis process, or by direct hydration present many similar problems and some problems which are unique to the specific process. The prime objective is to obtain a pure water azeotrope of ethyl alcohol (95.57% ethyl alcohol by weight). This can be accomplished by relatively simple distillation but the patent literature contains many distillation and equipment modifications (195-201). Some of these are specific for the removal of low boiling impurities (202-207) and others for the removal of higher boiling constituents (205, 208). Other patents refer to general purification procedures (209-213) and to the use of chemical treatment (214).

The odor of industrial alcohol can be improved by various methods (206) including contact with solid cuprous oxide (or cupric nitrate) (215) or a bed of sand (216). Liquid phase hydrogenation for less than 24 minutes at 20-45°C and up to 50 psi with a nickel catalyst is claimed to remove odor without increasing organic impurities (217).

Aldehydes (218, 219) and ketones (220) are removed by several different methods. For example, aqueous ethyl alcohol can be purified during distillation by first injecting an aqueous solution of sodium hydroxide into the alcohol stream. An aqueous solution of sodium bisulfite or sulfite sufficient to provide at least one mole of sulfite for each mole of aldehyde or ketone present is then injected into the combined stream, immediately prior to its entry into the rectifying column (221). Azeotropic distillation with benzene has been patented as a method for the removal of methyl ethyl ketone (220).

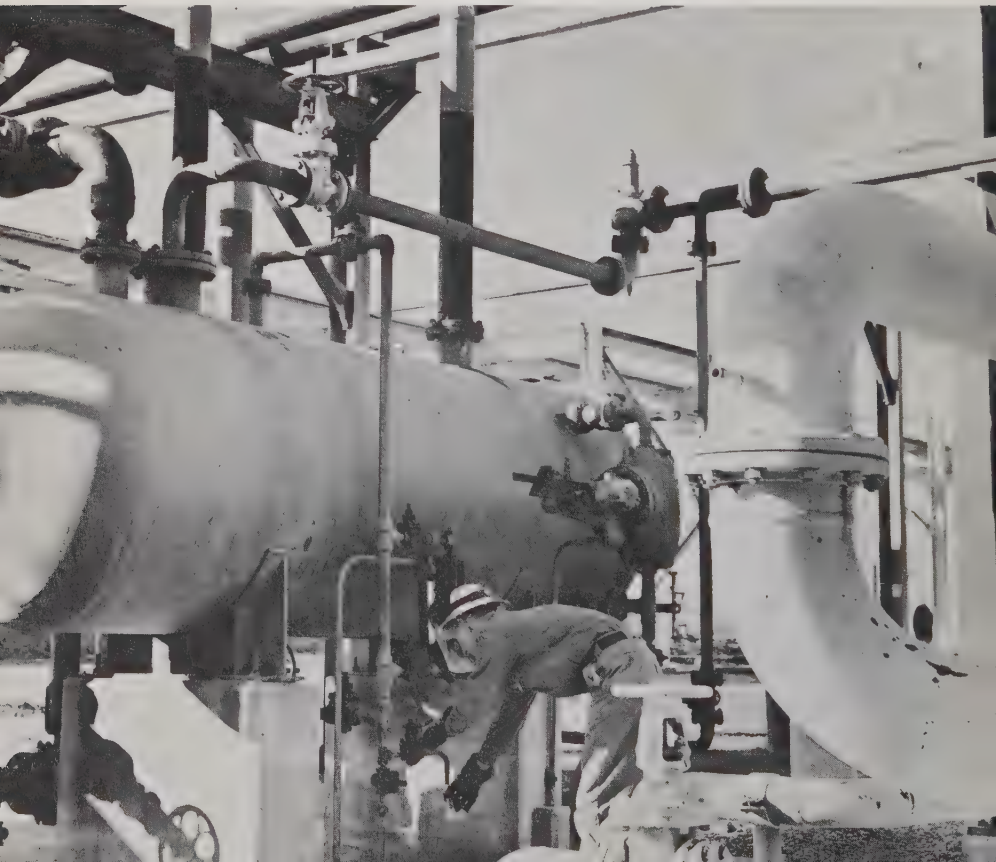
n-Propyl alcohol is removed from ethyl alcohol by extractive distillation with water (222). Ethyl alcohol is separated from a close-boiling mixture of the C₃ to C₆ alcohols or from the C₂ to C₈ aliphatic carbonyl compounds by distillation with a liquid reflux of the other components and sufficient salt solution (sodium acetate, sodium dihydrogen phosphate, lithium chloride or magnesium chloride) in the upper part of the distillation tower to maintain in the reflux at least 60 mole % of water and 1 to 10 mole % of the salt (223). The removal of aldehydes from ethyl alcohol intended for the preparation

of alcoholic potassium hydroxide can be effected by the addition of solid potassium hydroxide and metallic aluminum to the alcohol before distillation (224). Treatment of ethyl alcohol with mercuric chloride and sodium hydroxide will remove acetaldehyde and acetone (225).

Esterification-Hydrolysis Alcohol

The dilute alcohol vapors from the stripping column of the hydrolysis stage are passed to a scrubber where entrained sulfuric acid is neutralized by a sodium hydroxide solution. Alcohol, ethyl ether and water leave the scrubber overhead and are either condensed and stored as crude alcohol or sent to an ether still where the ethyl ether is

Drawing off an alcohol sample for analysis.



removed by live steam. The alcohol is then distilled to give the 95% alcohol of commerce.

Most of the patents noted in the introduction to this section, while general in scope, are related to the concentration and purification of synthetic alcohol produced by this process.

Direct Hydration Alcohol

The catalytic hydration of ethylene over an acid catalyst produces an initial product containing both acetaldehyde and entrained acid. The acetaldehyde is hydrogenated to ethyl alcohol. Ballard and Geyer have proposed an alternative process in which 0.1-3.0% by weight of potassium hydroxide is dissolved in the ethyl alcohol solution and the resulting solution is refluxed for at least 30 minutes before recovery of the alcohol by distillation (226).

Entrained acids may be neutralized by spraying the gaseous crude ethyl alcohol effluent with a solution of an alkaline material sufficient to give a pH of 6.5-7.5 (227). The effluent is then fractionated, condensed, hydrogenated to convert the aldehydes present, and redistilled.

The use of iron filings to remove phosphoric acid from aqueous ethyl alcohol has also been suggested (228).

Ether-free alcohol can be obtained by passing the hydration effluent without reduction of temperature or pressure into a column to which water has been added (229). Aqueous ethyl alcohol is recovered from the bottom of the still. The odor of ethyl alcohol produced by catalytic hydration is improved by contact in the vapor or liquid phase with sand (230).

Fermentation Alcohol

Industrial alcohol produced by the fermentation of molasses is obtained initially as an 8-10% solution. This solution (beer) is sent to an aldehyde still where aldehydes and other low boiling compounds are removed overhead. Ethyl alcohol is removed from the middle of the still and redistilled in a rectifying or refining column to give industrial alcohol. The fusel oils (amyl alcohols) are taken off farther down the column and water is discharged from the bottom of the column.

Most of the patent literature pertaining to impurities in fermentation alcohol relates to beverage alcohol. The removal of low boiling

impurities is especially important because of the presence of methyl alcohol. This alcohol can be removed by a two-stage rectification process in which the first column separates most of the water and the second stage gives an aqueous ethyl alcohol effluent at the bottom of the column and a methyl alcohol-containing ternary overhead (231). Extractive distillation with water has also been proposed (232, 233). Chemical treatment has been patented to remove esters (with alkali) (234), aldehydes and acids (with alkali superoxides) (235) and aldehydes and ketones (with reactive insoluble bisulfite-polyamine ion exchange resin) (236).

Alcohol from Carbon Monoxide and Hydrogen

The purification of ethyl alcohol obtained by a hydrocarbon synthesis process presents many problems because of the multiplicity of similar compounds produced at the same time. Extractive distillation with water has been proposed for the removal of isopropyl alcohol and other compounds (methyl ethyl ketone) which will form an azeotrope with it (237). A water concentration of 90-99 mole % is maintained throughout the column. An entraining liquid (benzene, *n*-heptane) can be used with water to separate ethyl alcohol from methyl propyl ketone (238). The ethyl alcohol is recovered overhead as its ternary azeotrope with water and the hydrocarbon. Methyl alcohol is separated by a combination of stripping and distillation (239).

Aldehydes can be removed by mixing the alcohol with an aqueous solution of water-soluble bisulfite having a pH of 6-8 and then distilling the alcohol from the resulting nonvolatile bisulfite addition products (240). A 0.01-1.0% mixture of succinic or malonic acid (or their low-molecular-weight esters) or ethyl acetoacetate may be used in a similar manner to remove oxidizable contaminants (241).

Absolute Alcohol

Simple distillation of an ethyl alcohol solution containing more than 4.43 wt % water will yield the azeotrope of ethyl alcohol and water [b.p. 78.15°C, 95.57 wt % (97.25 vol %, 89.43 mole %) ethyl alcohol]. Figure 5 gives the vapor-liquid composition curve for the alcohol-water system. Most of the uses of ethyl alcohol do not require dehydration beyond that of industrial alcohol (95 vol %) but for

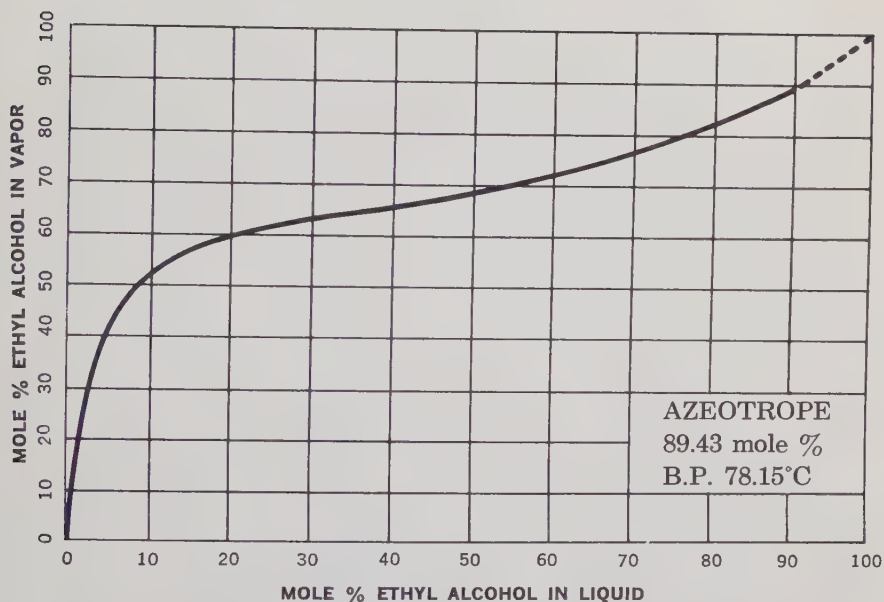


Figure 5. Vapor-liquid composition curve for the ethyl alcohol-water system at 760 mm Hg. (Courtesy of **Industrial and Engineering Chemistry**; based on data of P. N. Evans, *Ind. and Eng. Chem.*, **8**, 260-262; 1916; *ibid.*, **13**, 168-169, 1921.)

some solvent and chemical uses, absolute (anhydrous) ethyl alcohol is essential. The use of ethyl alcohol as a motor fuel, usually blended with a hydrocarbon fuel, also requires anhydrous alcohol. This has been of considerable importance in European and South American countries, but has never achieved equal importance in the United States. Absolute alcohol represents only a small percentage of the total alcohol production in this country.

The production of absolute alcohol can be conveniently divided into two general processes. In one process, the vapor pressure of the water is depressed and in the other, the vapor pressure of the water is increased (or the vapor pressure of the alcohol is depressed relative to that of the water). The first process is used for laboratory preparation and currently has little or no industrial applications. The second method utilizes a third component which is miscible with the alcohol but has a limited miscibility with water so that the partial vapor pressure of small amounts of water is enhanced. These liquids are

called entrainers and the process is one of azeotropic distillation.

The various methods which have been studied before 1937 for the dehydration of ethyl alcohol to absolute alcohol have been reviewed by Osborne, McKelvy and Bearce (242), Ellis (96) and Klar (243, 244). Klar (244) discusses the raw materials for the production of absolute alcohol and figures are given for its production in various countries. Manufacturing methods and types of apparatus are described in considerable detail with flow diagrams. Liquid versus solid drying agents, continuous versus batch methods along with relative costs are compared. A chronologically arranged bibliography of 187 references in the general literature, and another containing an additional classification on the basis of subject matter (containing 127 patent references) are given. Other references are those of Pique in 1925 (245), Guinot in 1926 (246), Mariller in 1927 (247), Pincass in 1928 on patent literature (248), Keyes in 1929 on azeotropic distillation (249), Dietrich in 1930 (250) and 1932 (251), Kilp in 1931 (252), Fritzweiler and Dietrich in 1934 (253), Klinga in 1934 (254), and Siedler in 1934 (255).

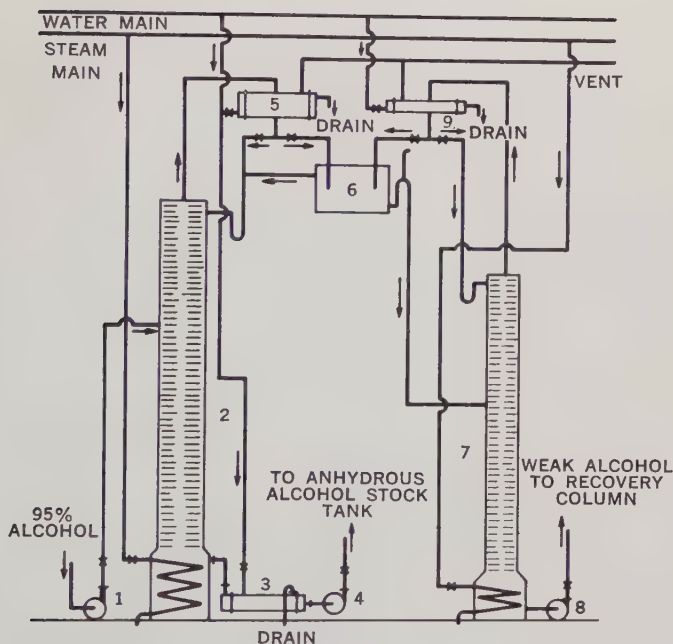
METHODS WHICH LOWER THE WATER VAPOR PRESSURE

The earliest method (1796) for the production of absolute alcohol utilized anhydrous potassium carbonate as the drying agent (4). Since that time a variety of inorganic compounds has been studied and patented. The following are typical: calcium oxide (lime), calcium carbide, calcium sulfate (256), calcium aluminum oxide (257, 258), aluminum and mercuric chloride, zinc chloride, potassium carbonate (in ethylene glycol) (259) and sodium hydroxide.

Scheibel has discussed the dehydration of ethyl alcohol by fractional liquid extraction (260, 261). This process is a combination of the vapor pressure lowering (of water) and the utilization of the solubility properties of ethyl alcohol and water. Their solubilities are sufficiently different to permit separation by any immiscible pair of solvents which do not react with the alcohol or water.

AZEOTROPIC DISTILLATION

The first application of dehydration by azeotropic distillation was the dehydration of ethyl alcohol by the formation of a ternary azeotrope with benzene (1902) (5, 6) and the process is still used because of its efficiency and low cost. The ternary azeotrope boils at 64.85°C and contains 7.5 wt % (23.3 mole %) water, 18.5 wt % (22.8 mole



Item	Description	Material	Specification
1	Feed pump	Bronze	30 g.p.h., 70 ft. head, 2 h.p. motor, flameproof, spare pump installed
2	Azeotropic column	Copper	4 ft. diam., 60 ft. high, 55 plates, feed on 40th plate, boiler 250 sq. ft. tube area
3	Product cooler	Copper	12 tubes, 1 in. diam. X 6 ft. lg., 3-pass water in jacket
4	Product pump	Bronze	300 g.p.h., 70 ft. head, 2 h.p. motor, flameproof, spare pump installed
5	Condenser	Copper	54 tubes, 2 in. diam. X 8 ft. long, cooling water through tubes, 3-pass
6	Decanter	Copper	Horizontal cylindrical vessel, 4 ft. diam. X 6 ft. long
7	Benzene recovery column	Copper	1 ft. 6 in. diam. X 40 ft. high, 40 plates, feed 30th plate, boiler 30 sq. ft. tube area
8	Weak alcohol pump	Bronze	100 g.p.h., 80 ft. head, 1 h.p. motor, flameproof, spare installed
9	Condenser	Copper	18 tubes, 2 in. diam. X 8 ft. long, water through tubes, 3-pass

Figure 6. Flowsheet for the dehydration of industrial alcohol to absolute alcohol using benzene as the entraining agent. (From W. S. Norman, *International Chem. Eng.*, 31, 499, 1950. By permission of the publishers: Lomond Technical Press Ltd.)

%) ethyl alcohol and 74.0 wt % (53.9 mole %) benzene (262-264). Anhydrous ethyl alcohol is drawn off from the bottom of the column. The distillate of the ternary azeotrope separates into two layers. The upper layer contains 84.5% benzene, 14.5% ethyl alcohol and 1.0% water and is returned to the column. The lower layer, which is sent to a stripper column for benzene recovery, consists of 11% benzene, 53% alcohol and 36% water. Figure 6 gives a flow sheet for a typical dehydration process using benzene as the entraining agent (265).

Norman has published vapor-liquid equilibrium measurements for the system ethyl alcohol-benzene-water. He correlated his data by plotting the activity coefficients of the three components and the results are consistent with the Gibbs-Duhem equation (266).

Ethyl ether can also be used as an entrainer for the production of absolute alcohol (267-272). It forms a binary azeotrope with water, (b.p. 34.15°C, 1.25 wt % water) but not with ethyl alcohol and it does not form a ternary azeotrope with water and ethyl alcohol. Methylene chloride may be used in a process similar to that for ethyl ether for it also forms a binary with water but no ternary with water and ethyl alcohol (273). Many other compounds have been suggested for use in the dehydration of ethyl alcohol by azeotropic distillation. These include isobutylene (274), isooctane (274), gasoline (275), benzene and naphtha (276, 277), isopropyl ether (278), methyl alcohol (279) and acetone (279). The Drawinol process uses trichlorethylene (280, 281).

ANALYSIS

The analysis of ethyl alcohol for impurities and the qualitative and quantitative determination of ethyl alcohol in many different substances has occupied the chemist for as long as there has been chemistry. The development of modern laboratory instruments has led to increasingly simple and accurate procedures for ethyl alcohol analysis. For example, the infrared spectrophotometer permits very rapid identifications to be made. Gas chromatography promises to become increasingly important.

Some general and some recent references to the analysis and identification of ethyl alcohol are noted here; a complete resume would require more space than is justified in a general discussion of ethyl alcohol.

Miscellaneous Analytical Procedures

Infrared spectra (282, 283).

Assignment of the OH bending frequency (284).

OH and OD deformation bands (285).

Temperature dependence of OH frequency shifts and OH band intensities (286).

Infrared spectrometric study of molecular association (287).

Light absorption of water-alcohol solutions in the near infrared spectrum range (288).

Conversion to ethyl nitrite and subsequent oxidation (289).

Detection of traces of benzene (290, 291).

Estimation of mixtures of ethyl alcohol and methyl alcohol (292).

Detection and approximate estimation of methyl, isopropyl and amyl alcohols in ethyl alcohol (293).

Formation of potassium ethyl xanthate (m.p. 215.3°C) (294).

Refractometric method for rapid determination of ethyl alcohol in tinctures (295).

Determination by use of porcelain microdiffusion cells (296).

Catalytic oxidation to acetaldehyde and estimation of the acetaldehyde with nitroprusside (297).

Polarographic method for determining aldehydes in ethyl alcohol (298).

Polarographic determination of impurities in ethyl alcohol (299).

Quantitative analysis by gas-liquid partition chromatography of solutions of ethyl alcohol-water-ethyl ether, ethyl alcohol-water and ethyl alcohol-chloroform (300).

Separation of ethyl alcohol from methyl and ethyl mercaptan by GLPC (301).

Determination of acid and esters in industrial alcohol (302).

Mass spectrum (303).

Ultra-violet absorption and determination of small amounts of benzene (304).

The determination of ethyl alcohol in ethyl ether (305).

Improved permanganate time test for control of ethyl alcohol quality (306).

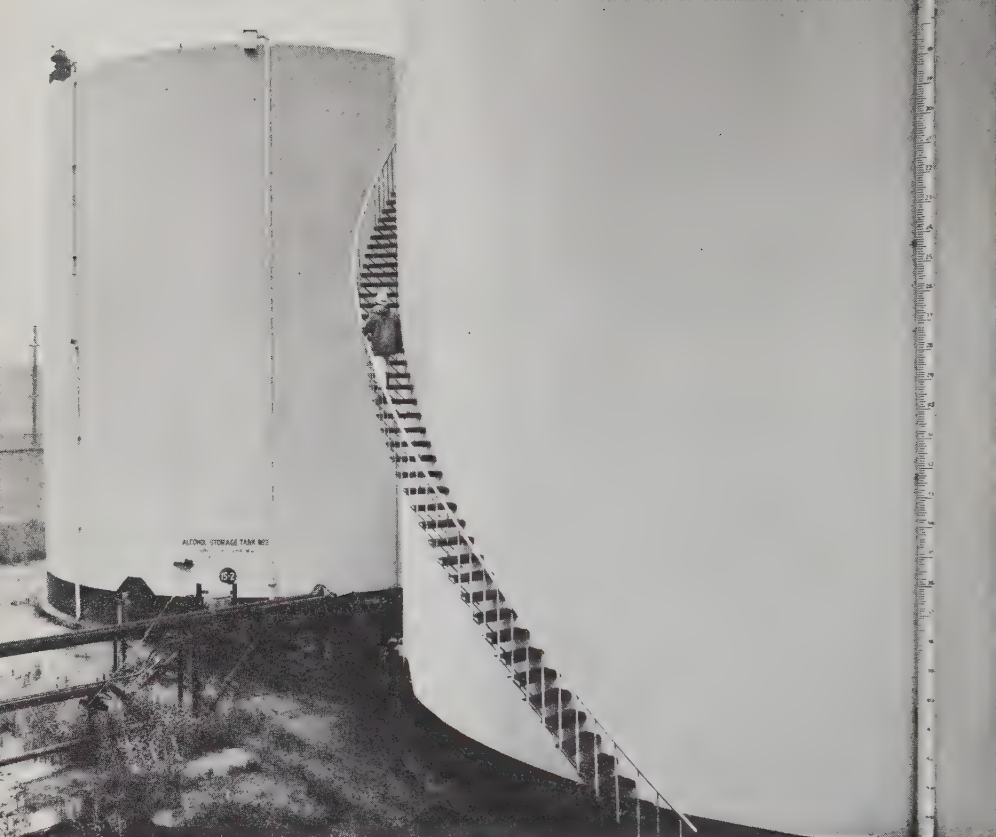
STORAGE AND HANDLING

Steel tanks, piping and equipment are generally recommended for the storage and handling of pure or denatured ethyl alcohol. Ethyl alcohol is not normally corrosive to metals, however, and other materials of construction such as iron, copper or brass may also be used. It should be kept in mind that brass may be corroded by the ammonia denaturant present in S.D.A. 36.

The corrosive action of industrial alcohol on rubber, steel, silicones, carbon, graphite, aluminum, lead, iron, nickel, nickel alloys, tantalum, and various types of protective coatings was the subject of a symposium reported in *Chemical Engineering* in 1948 (307). Moore has reported on the corrosive action of industrial alcohol on construction materials (308). At temperatures up to its boiling point, pure ethyl alcohol is probably less corrosive toward iron, steel and copper than any other common liquid. If, however, couple effects can be set up between two or more of these metals in the presence of air in aqueous solutions, corrosion may occur at elevated temperatures. Ethyl alcohol is a corrosive agent at elevated temperatures toward aluminum and magnesium because of the ease with which they form ethylates. This action is increased markedly by the presence of mercury or its alcohol-soluble salts. Ethyl alcohol may become highly active toward metals if it becomes contaminated during a manufacturing or recovery process.

Tanks for storage of ethyl alcohol may be located either above or below ground. Above-ground tanks should generally be located fifty feet or more from buildings and should be surrounded by a dike. Underground tanks should generally be located at least five feet away from building foundations and should be coated with a corrosion-resistant material. All tanks should be suitably vented and each vent pipe should be protected with a flame arrestor.

Tanks should be calibrated and equipped with an accurate measuring device. One often-used device employs an internal float and chain which pulls an indicator along a gauge board on the outside of the tank. An open-cup thermometer may be lowered into the tank to determine the temperature of the alcohol.



Top. Storage tanks for ethyl alcohol at Carteret, New Jersey.

Bottom. Loading ethyl alcohol into tank cars.



Pumps for handling ethyl alcohol should preferably be of the centrifugal, self-priming type, with spark-proof electric motor drives. Standard valves, gaskets and valve packings may be used. All equipment, pipe lines and tanks should be grounded as a protection against static electricity.

Ethyl alcohol is shipped in tank cars, tank trucks, 55-gallon steel drums and a variety of smaller containers. In addition, special resin-lined containers are used to ship certain types of denatured alcohol. Ethyl alcohol is classed as a flammable liquid and Interstate Commerce Commission regulations require a red caution label on all shipping containers. The shipment, storage and handling of industrial ethyl alcohol are regulated by the Alcohol and Tobacco Tax Division of the Internal Revenue Service, U.S. Treasury Department (309, 310).

TOXICITY OF ETHYL ALCOHOL

Ethyl alcohol depresses the functions of the central nervous system, primarily by its action on the brain. When using denatured ethyl alcohol, consideration should also be given to the toxic effects of the various noxious materials present as denaturants. The discussion which follows concerns only pure ethyl alcohol.

Hazard from Inhalation

The toxic hazard of industrial exposure to ethyl alcohol vapor is low because vapor concentrations cannot reach anesthetic levels without odor and sensory irritation becoming intolerable. The minimum odor threshold has been reported at 350 ppm (0.658 mg/l). Repeated or prolonged exposure to low concentrations of ethyl alcohol vapor in air apparently have no chronic toxic effect on man. A maximum allowable concentration (MAC) of 1,000 ppm (1.88 mg/l) has been established for daily eight-hour exposure to the vapor.

Table IV
ETHYL ALCOHOL CONCENTRATION
AND ITS EFFECTS IN MAN¹

Concentration		Effects in Man ²
mg/liter	ppm	
10-20	5,320-10,640	Some transient coughing and smarting of the eyes and nose which disappear after 5 to 10 minutes; not comfortable but tolerable.
30	15,960	Continuous lachrymation and marked coughing; could be tolerated but with discomfort.
40	21,280	Just tolerable for short periods.
More than 40	More than 21,280	Intolerable and suffocating for even short periods.

¹ From "Statement of Toxicity" prepared by the Medical Research Division, Esso Research and Engineering Co., Linden, New Jersey.

² These observations were made on men at rest; at higher breathing rates, irritation would become intolerable at lower vapor concentrations.

Symptoms of intoxication or inebriation generally will not occur unless concentrations exceed 8,000 ppm (15 mg/l), and then only after several hours of exposure. Concentrations of about 5,000-11,000 ppm cause some transient coughing and irritate the eyes and nose (Table IV). This irritation, which is tolerable but not comfortable, will disappear after 5 to 10 minutes. At about 16,000 ppm there are continuous coughing and lachrymation which can be tolerated, but with discomfort. Higher levels are tolerable only for short periods; a concentration of about 21,000 ppm is immediately intolerable and suffocating. The massive concentrations required to cause loss of consciousness would be encountered only by accident, since sensory irritation at these levels would be overwhelming.

Hazard from Ingestion

Ingestion of ethyl alcohol at a rate greater than one ounce of 100 proof whiskey (50% alcohol) per hour results in increasing blood alcohol levels, incoordination and inebriation. At very high intake levels, these effects can be followed by coma and death from respiratory and heart failure. Blood alcohol levels of 550 mg/100 ml are usually fatal to man if treatment is not instituted promptly. This level could be reached after drinking a single dose of about 3 grams of alcohol per kilogram of body weight—or approximately one pint of 100 proof whiskey, taken all at once. Deaths have also been reported at levels of 350 mg/100 ml. The universally accepted blood level above which it is unsafe to operate a motor vehicle is 50 mg/100 ml.

At the present time there is no clear understanding of the systemic effects of longtime excessive ethyl alcohol ingestion. However, the observed incidence of cirrhosis of the liver in alcoholics is described as being at least 6 times as high as that in non-alcoholics, and the death rate from this disease correlates closely in many areas with the per capita consumption of alcoholic beverages. Nutritional deficiencies frequently observed in alcoholics may be the result of decreased food intake over long periods rather than a direct toxic effect of alcohol.

Hazard from Skin Contact

Ethyl alcohol is not absorbed significantly through the skin. Continuous daily contact with ethyl alcohol may dry and de-fat the skin, however, making it susceptible to dermatitis. Ethyl alcohol is irritating to the eyes in both liquid and vapor form.

Precautions

Atmospheric concentrations of ethyl alcohol vapor should be kept below the suggested MAC of 1,000 ppm for daily eight-hour exposures. The eyes should be protected from splashes and excessive skin contact should be avoided.

The presence of denaturants in industrial ethyl alcohol renders it unfit for human consumption.

First Aid

Remove the person affected from the contaminated area. Administer artificial respiration and oxygen if breathing is irregular or has stopped. Call a physician if exposure is severe enough to cause unconsciousness. Irrigate the eyes with water.

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INDUSTRIAL ALCOHOL

Ethyl alcohol has been an important source of tax revenue for every civilized country since taxation was discovered. At first beverage and industrial alcohols were taxed equally; but as ethyl alcohol became a more important industrial chemical, the tax was removed. The first law making industrial alcohol tax free was passed in England in 1855. It was apparent at the time that some of this alcohol might be misdirected into beverage outlets so the principle of denaturation was introduced. The object was to add substances to the alcohol which would not interfere with its industrial use but which would make the alcohol unfit as a beverage. The first denatured alcohol was a mixture of 90% ethyl alcohol and 10% wood naphtha called "methylated" spirits.

Other countries soon followed England's lead and by 1890 denatured, tax-free alcohol was well established in Europe. The United States did not pass the required legislation to permit the denaturing of ethyl alcohol until 1906 although Congress in 1897 was advised that "the use of alcohol for industry is legitimate and necessary. There is scarcely a manufacturer who does not use alcohol in the production of his goods." The use of ethyl alcohol by industry in the United States increased rapidly from 1906 until at present it is considered the most important synthetic oxygenated organic compound.

Federal regulations governing the production, distribution and use of industrial alcohol are contained in Title 26 (1954), Code of Federal Regulations. The text of these regulations has been published by the Internal Revenue Service of the U.S. Treasury Department in a series of booklets which can be obtained from the U.S. Government Printing Office, Washington 25, D.C. (309-314).

Denaturants

Table V lists the 95 substances presently authorized by government regulations as denaturants for ethyl alcohol. In addition, if it can be shown that none of the authorized substances can be used in the manufacture of a particular product, the use of other substances may be authorized by the Alcohol and Tobacco Tax Division of the

Table V
AUTHORIZED DENATURANTS
for Specially Denatured Alcohol (S.D.A.)
and Completely Denatured Alcohol (C.D.A.)
(312)

Acetaldehyde	S.D.A. 29.
Acetone N.F.	S.D.A. 23-A; 23-H.
Acetaldol	C.D.A. 18.
Almond oil, bitter N.F.	S.D.A. 38-B.
Ammonia, aqueous	S.D.A. 36.
Ammonia solution, strong U.S.P.	S.D.A. 36.
Anethole U.S.P.	S.D.A. 38-B.
Anise oil U.S.P.	S.D.A. 38-B.
Bay oil (myrcia oil) N.F.	S.D.A. 23-F; 38-B; 39-D.
Benzaldehyde N.F.	S.D.A. 38-B.
Benzene	S.D.A. 2-B; 2-C; 12-A.
Bergamot oil N.F.	S.D.A. 23-F; 38-B.
Bone oil (Dipple's oil)	S.D.A. 17.
Boric acid U.S.P.	S.D.A. 38-F.
Brucine alkaloid	S.D.A. 40.
Brucine sulfate N.F. IX	S.D.A. 40.
n-Butyl alcohol	S.D.A. 44.
tert-Butyl alcohol	S.D.A. 39; 39-A; 39-B; 40; 40-A.
Camphor U.S.P.	S.D.A. 27; 27-A; 38-B.
Caustic soda, liquid	S.D.A. 36.
Cedar leaf oil U.S.P. XIII	S.D.A. 38-B.
Chloroform	S.D.A. 20.
Chlorothymol N.F.	S.D.A. 38-B; 38-F.
Cinchonidine	S.D.A. 39-A.
Cinchonidine sulfate N.F. IX	S.D.A. 39-A.
Cinnamic aldehyde (cinnamaldehyde) N.F. IX.	S.D.A. 38-B.
Cinnamon oil (cassia oil) U.S.P.	S.D.A. 38-B.
Citronella oil, natural	S.D.A. 38-B.
Clove oil U.S.P.	S.D.A. 27-A; 38-B.
Coal tar U.S.P.	S.D.A. 38-B.
Diethyl phthalate	S.D.A. 39-B; 39-C.
Ethyl acetate	S.D.A. 35; 35-A.
Ethyl ether	S.D.A. 13-A; 19; 32.
Eucalyptol U.S.P.	S.D.A. 37; 38-B.
Eucalyptus oil N.F.	S.D.A. 38-B.
Eugenol U.S.P.	S.D.A. 38-B.
Formaldehyde solution U.S.P.	S.D.A. 22; 38-C; 38-D.
Gasoline	S.D.A. 28-A.
Glycerol U.S.P.	S.D.A. 31-A.
Guaiacol N.F.	S.D.A. 38-B.
Iodine U.S.P.	S.D.A. 25; 25-A.
Kerosene	C.D.A. 18; 19.
Lavender oil U.S.P.	S.D.A. 27-B; 38-B.
Menthol, U.S.P.	S.D.A. 37; 38-B; 38-C; 38-D; 38-F.
Mercuric iodide, red N.F.	S.D.A. 42.
Methyl alcohol	S.D.A. 3-A; 30.
Methylene blue N.F.	S.D.A. 4; S.D.R. 4.

Table V (continued)
AUTHORIZED DENATURANTS
for Specially Denatured Alcohol (S.D.A.)
and Completely Denatured Alcohol (C.D.A.)

Methyl isobutyl ketone	C.D.A. 18; 19; S.D.A. 23-H.
Methyl violet (methylosaniline chloride)	S.D.A. 33.
Methyl violet (methylosaniline chloride) U.S.P.	S.D.A. 33.
Mustard oil, volatile (allyl isothiocyanate), U.S.P. XII	S.D.A. 38-B.
Nicotine solution	S.D.A. 4; S.D.R. 4.
Peppermint oil U.S.P.	S.D.A. 38-B.
Phenol U.S.P.	S.D.A. 38-B; 46.
Phenyl mercuric benzoate	S.D.A. 42.
Phenyl mercuric chloride N.F. IX	S.D.A. 42.
Phenyl mercuric nitrate N.F.	S.D.A. 42.
Phenyl salicylate (salol) N.F.	S.D.A. 38-B.
Pine needle oil, dwarf N.F.	S.D.A. 38-B.
Pine oil, N.F.	S.D.A. 38-B.
Pine tar, N.F.	S.D.A. 3-B.
Potassium iodide, U.S.P.	S.D.A. 25; 25-A; 42.
Pyridine bases	S.D.A. 6-B.
Pyronate	C.D.A. 18.
Quassia, fluid extract, N.F. VII	S.D.A. 39.
Quassin	S.D.A. 40.
Quinine N.F.	S.D.A. 39-A.
Quinine bisulfate N.F.	S.D.A. 39-A; 39-D.
Quinine hydrochloride U.S.P.	S.D.A. 39-A.
Quinine sulfate U.S.P.	S.D.A. 39-D.
Resorcin U.S.P.	S.D.A. 23-F.
Rosemary oil N.F.	S.D.A. 27; 38-B.
Rubber hydrocarbon solvent	S.D.A. 2-B; 2-C.
Safrol	S.D.A. 38-B.
Salicylic acid U.S.P.	S.D.A. 23-F; 39.
Sassafras oil N.F.	S.D.A. 38-B.
Shellac (refined)	S.D.A. 45.
Soap, hard N.F.	S.D.A. 31-A.
Soap, medicinal soft U.S.P.	S.D.A. 27-B.
Sodium iodide, U.S.P.	S.D.A. 25; 25-A.
Sodium, metallic	S.D.A. 2-C.
Sodium salicylate U.S.P.	S.D.A. 39; 39-D.
Spearmint oil N.F.	S.D.A. 38-B.
Spearmint oil, terpeneless	S.D.A. 38-B.
Spike lavender oil, natural	S.D.A. 38-B.
Storax U.S.P.	S.D.A. 38-B.
Sucrose octa-acetate	S.D.A. 40-A.
Thimerosal N.F.	S.D.A. 42.
Thyme oil N.F.	S.D.A. 38-B.
Thymol N.F.	S.D.A. 37; 38-B; 38-F.
Tolu balsam U.S.P.	S.D.A. 38-B.
Turpentine oil N.F.	S.D.A. 38-B.
Vinegar	S.D.A. 18.
Wintergreen oil (methyl salicylate) U.S.P.	S.D.A. 38-B; 46.
Wood alcohol	S.D.A. 1.

Internal Revenue Service. Actually only a few denaturants are used in large volume. The two most important are acetaldehyde and wood alcohol. Other leading denaturants are benzene, pure methyl alcohol, brucine, *tert*-butyl alcohol, ethyl acetate, ethyl ether, acetone and methyl isobutyl ketone.

The denaturant used in industrial alcohol intended for conversion into a chemical derivative is often the same as the chemical that the alcohol is intended to produce. Thus, acetaldehyde is the denaturant for specially denatured alcohol Formula No. 29, whose principal use is as a raw material in the synthesis of acetaldehyde. Wood alcohol and pure methyl alcohol are used extensively because their chemical properties are similar to those of ethyl alcohol, which makes these denaturants difficult to remove while remaining acceptable for chemical applications. Essential oils and drugs serve as denaturants in many denatured alcohol formulas. These formulas are usually authorized for use in cosmetics and pharmaceuticals which include the same essential oils and drugs in their formulations.

In general, denaturants possess distinctive odors and are difficult to remove by physical or chemical means. They are usually low in cost and are readily available in commercial quantities.

Specially Denatured Alcohol (S.D.A.)

Specially denatured alcohol is by far the most widely used form of industrial ethyl alcohol. During the fiscal year ending June 30, 1961, the production of specially denatured alcohol totalled slightly over 288 million wine gallons, accounting for over 95% of the industrial alcohol produced. Table VI lists withdrawals of specially denatured alcohol, by formula, for fiscal year 1960, along with the authorized composition of each formula.

Specially denatured alcohol is generally available commercially in both 190 proof and 200 proof (anhydrous) grades. Certain formulas, because of the type of denaturant employed or because of specialized end uses, are only available in a single grade. The properties of each S.D.A. formula will of course depend upon the particular denaturants used in it.

The largest single use for specially denatured alcohol is as a raw material in the production of acetaldehyde. During fiscal year 1960, 156.3 million gallons of alcohol out of a total consumption of 283.5

million gallons were used for this purpose. Acetic acid, vinegar, ethyl ether, ethyl acetate and ethyl chloride are among the many other compounds manufactured with specially denatured alcohol. As a solvent, specially denatured alcohol is used in the manufacture of cosmetics, pharmaceuticals, surface coatings, detergents, plastics, adhesives, inks and many other products.

Table VI

**WITHDRAWALS DURING FISCAL YEAR 1960 AND
COMPOSITIONS OF SPECIALLY DENATURED ALCOHOLS**

S.D.A. Formula No.	Withdrawals, in wine gallons ¹	Authorized Compositions ²
		To every 100 gallons of ethyl alcohol, add:
1	26,517,934	Five gallons of wood alcohol.
2-B	23,585,510	One-half gallon of benzene or one-half gallon of rubber hydrocarbon solvent.
2-C	8,548	Thirty-three pounds, or more, of metallic sodium and either one-half gallon of benzene or one-half gallon of rubber hydrocarbon solvent.
3-A	10,925,471	Five gallons of methyl alcohol.
3-B	55	One gallon of pine tar N.F.
4	1,156,398	One gallon of the following solution: five gallons of an aqueous solution containing 40 per cent nicotine; and 3.6 av. ounces of methylene blue, N.F.; water sufficient to make 100 gallons.
6-B	39,286	One-half gallon of pyridine bases.
12-A	107,164	Five gallons of benzene.
13-A	39,615	Ten gallons of ethyl ether.
17	3,607,499	Five-hundredths (0.05) gallon (6.4 fluid ounces) of bone oil (Dipple's oil).
18	6,450,798	One hundred gallons of vinegar of not less than 90-grain strength or one hundred and fifty gallons of vinegar of not less than 60-grain strength.
19	44,554	One hundred gallons of ethyl ether.
20	11,017	Five gallons of chloroform.
22	108	Ten gallons of formaldehyde solution (U.S.P.).
23-A	551,729	Ten gallons of acetone, N.F.
23-F	265	Three pounds of salicylic acid, U.S.P.; one pound of resorcin, U.S.P.; and one gallon of bergamot oil, N.F. or bay oil, N.F.
23-H	2,026,027	Eight gallons of acetone, N.F. and 1.5 gallons of methyl isobutyl ketone.
25	10,186	Twenty pounds of iodine, U.S.P., and 15 pounds of either potassium or sodium iodide, U.S.P.

Table VI (continued)

WITHDRAWALS DURING FISCAL YEAR 1960 AND
COMPOSITIONS OF SPECIALLY DENATURED ALCOHOLS

S.D.A. Formula No.	Withdrawals, in wine gallons ¹	Authorized Compositions ²
		To every 100 gallons of ethyl alcohol, add:
25-A	23,700	A solution composed of 20 pounds of iodine, U.S.P., 15 pounds of potassium or sodium iodide, U.S.P. and 15 pounds of water.
27	15,891	One gallon of rosemary oil, N.F. and 30 pounds of camphor, U.S.P.
27-A	1,298	Thirty-five pounds of camphor, U.S.P. and one gallon of clove oil, U.S.P.
27-B	75,099	One gallon of lavender oil, U.S.P. and 100 pounds of medicinal soft soap, U.S.P. NOTE: the requirements of this formula may be met by adding one gallon of lavender oil, U.S.P. and 66.5 pounds of U.S.P. quality soap concentrate containing 25 per cent water to 100 gallons of alcohol and, after mixing, by adding thereto 33.5 pounds of water and again mixing.
28-A	28	One gallon of gasoline.
29	172,935,418	One gallon of 100 per cent acetaldehyde or 5 gallons of an alcohol solution of acetaldehyde containing not less than 20 per cent acetaldehyde or, where approved by the Director as to material and quantity, not less than 6.8 pounds, if solid, or 1 gallon, if liquid, of any chemical. Where material other than acetaldehyde is proposed to be used, the applicant shall furnish the Director with specifications and duplicate 8 ounce samples.
30	2,421,450	Ten gallons of methyl alcohol.
31-A	³	One hundred pounds of glycerol, U.S.P. and 20 pounds of hard soap, N.F.
32	2,142,910	Five gallons of ethyl ether.
33	716	Thirty pounds of methyl violet or methyl violet, U.S.P.
35	17,579	Thirty-five gallons of ethyl acetate.
35-A	9,882,452	4.26 gallons of ethyl acetate having an ester content of 100 per cent by weight or the equivalent thereof not to exceed 5 gallons of ethyl acetate with an ester content of not less than 85 per cent by weight.
36	4,384,471	Three gallons of ammonia, aqueous, 27 to 30 per cent by weight; three gallons of strong ammonia solution, U.S.P.; 17.5 pounds of caustic soda, liquid grade, containing 50 per cent sodium hydroxide by weight; or 12.0 pounds of caustic soda, liquid grade, containing 73 per cent sodium hydroxide by weight.

Table VI (continued)

WITHDRAWALS DURING FISCAL YEAR 1960 AND COMPOSITIONS OF SPECIALLY DENATURED ALCOHOLS

S.D.A. Formula No.	Withdrawals, in wine gallons ¹	Authorized Compositions ² To every 100 gallons of ethyl alcohol, add:
37	1,536,312	Forty-five fluid ounces of eucalyptol, U.S.P., 30 av. ounces of thymol, N.F., and 20 av. ounces of menthol, U.S.P.
38-B	895,421	Ten pounds of one or a total of 10 pounds of two or more of the oils and substances listed below:
		Anethol, U.S.P. Anise oil, U.S.P. Bay oil (myrcia oil), N.F. Benzaldehyde, N.F. Bergamot oil, N.F. Bitter almond oil, N.F. Camphor, U.S.P. Cedar leaf oil, U.S.P. XIII Chlorothymol, N.F. Cinnamic Aldehyde, N.F. IX Cinnamon oil (cassia oil), U.S.P. Citronella oil, (natural) Clove oil, U.S.P. Coal tar, U.S.P. Eucalyptol, U.S.P. Eucalyptus oil, N.F. Eugenol, U.S.P. Guaiacol, N.F. Lavender oil, U.S.P. Menthol, U.S.P.
		Mustard oil, volatile (allyl isothiocyanate), U.S.P. XII Peppermint oil, U.S.P. Phenol, U.S.P. Phenyl salicylate (salol), N.F. Pine oil, N.F. Pine needle oil, dwarf, N.F. Rosemary oil, N.F. Safrol Sassafras oil, N.F. Spearmint oil, N.F. Spearmint oil, terpeneless Spike lavender oil, natural Storax, U.S.P. Thyme oil, N.F. Thymol, N.F. Tolu balsam, U.S.P. Turpentine oil, N.F. Wintergreen oil (methyl salicylate), U.S.P.
		Where it is shown that none of the above single denaturants or combinations can be used in the manufacture of a particular product, application may be made to use another essential oil or substance having denaturing properties satisfactory to the Director. In such case, the applicant shall furnish the Director with specifications and duplicate 8 ounce samples for examination.
38-C	58,611	Ten pounds of menthol, U.S.P., and 1.25 gallons of Formaldehyde solution, U.S.P.
38-D	14,856	Two and one-half pounds of menthol, U.S.P. and 2.5 gallons of Formaldehyde solution, U.S.P.
38-F	28,977	(1) Six pounds of boric acid, U.S.P., 1½ pounds thymol, N.F., 1½ pounds chlorothymol, N.F., and 1½ pounds menthol, U.S.P.; or (2) seven pounds of boric acid, U.S.P. and a total of 3 pounds of any two or more denaturing materials listed under Formula No. 38-B.
39	145	Nine pounds of sodium salicylate or salicylic acid, U.S.P., 1.25 gallons fluid extract of quassia, N.F. VII and ½ gallon of tert-butyl alcohol.

Table VI (continued)
WITHDRAWALS DURING FISCAL YEAR 1960 AND
COMPOSITIONS OF SPECIALLY DENATURED ALCOHOLS

S.D.A. Formula No.	Withdrawals, in wine gallons ¹	Authorized Compositions ² To every 100 gallons of ethyl alcohol, add:
39-A	21	Sixty av. ounces of any one of the following alkaloids or salts together with $\frac{1}{8}$ gallon of tert -butyl alcohol: Quinine, N.F., Quinine bisulfate, N.F., Quinine hydrochloride, U.S.P., Cinchonidine, or Cinchonidine sulfate, N.F. IX.
39-B	43,961	Two and one-half gallons of diethyl phthalate and $\frac{1}{8}$ gallon of tert -butyl alcohol.
39-C	1,672,255	One gallon of diethyl phthalate.
39-D	1,200	One gallon of bay oil, N.F. and either 50 av. ounces of quinine sulphate, U.S.P., 50 av. ounces of quinine bisulphate, N.F., or 200 av. ounces of sodium salicylate, U.S.P.
40	11,115,024	One and one-half av. ounces of brucine (alkaloid), brucine sulfate (N.F. IX), or quassin, and $\frac{1}{8}$ gallon of tert -butyl alcohol.
40-A	21,663	Five pounds of sucrose octa-acetate and $\frac{1}{8}$ gallon of tert -butyl alcohol.
42	12,279	(1) Eighty grams of potassium iodide, U.S.P. and 109 grams of red mercuric iodide, N.F.; or (2) ninety-five grams of thimerosal, N.F.; or (3) seventy-six grams of any of the following: phenyl mercuric nitrate, N.F.; phenyl mercuric chloride, N.F. IX, or phenyl mercuric benzoate.
44		Ten gallons of n -butyl alcohol.
45	41,236	Three hundred pounds of refined white or orange shellac.
46	1,360	Twenty-five fluid ounces of phenol, U.S.P. and 4 fluid ounces of wintergreen oil (methyl salicylate), U.S.P.
—	183,371	Special formula.
Total . . .	282,609,868 ⁴	

¹ From "Statistics Relating To The Alcohol And Tobacco Industries, Fiscal Year Ended June 30, 1960," U.S. Treasury Department, Internal Revenue Service Publication No. 67 (1960), page 35.

² From "Formulas For Denatured Alcohol, Part 212 of Title 26, Code of Federal Regulations," U.S. Treasury Department, Internal Revenue Service Publication No. 368 (with T.D. 6474).

³ Not reported.

⁴ Includes 1,050,632 wine gallons withdrawn for use of the United States and 3,731 withdrawn for export.

HYDROUS
ALCOHOL
TANK No 4
8194 WG
PER INCH

M-4

SDA 39-C
DENATURED ALCOHOL
MIX & STORAGE TANK
CAPACITY 12,181.48
49.02 GALS. PER INCH

Table VII lists the products and processes in which government regulations authorize specially denatured alcohol to be used. Generally, more than one S.D.A. formula is authorized for each use. This allows a manufacturer to select that formula which contains denaturants best suited to the particular product or process he has in mind. Each product and process is assigned a code number by the Alcohol and Tobacco Tax Division. These code numbers are called for on certain report forms which must be submitted by the user.

Specially denatured alcohol is unfit for beverage purposes. It is therefore not subject to Federal tax. It can only be sold, however, to those persons who have been issued an industrial use permit and a withdrawal permit by the Alcohol and Tobacco Tax Division. To obtain these permits, prospective users must meet the qualifications set forth in Part 211 of Title 26 (1954), Code of Federal Regulations (309). Various forms must be submitted to the Alcohol and Tobacco Tax Division and a bond must be filed. After the permits have been issued, each user must maintain records of receipt, storage and disposition of all the alcohol he receives.

Table VII
AUTHORIZED USES OF
SPECIALLY DENATURED ALCOHOL¹
(312)

Product or process	Code No.	Formulas authorized
Acetaldehyde	551	1, 2-B, 29.
Acetic acid	512	1, 2-B, 29, 35-A.
Adhesives and binders	036	1, 3-A, 12-A, 23-A, 30.
Aldehydes, miscellaneous	552	1, 2-B, 29.
Alkaloids (processing)	344	1, 2-B, 2-C, 3-A, 12-A, 13-A, 17, 23-A, 30, 32, 35-A.
Animal feed supplement	910	35-A.
Antibiotics (processing)	343	1, 2-B, 3-A, 12-A, 13-A, 23-A, 30, 32, 35-A.
Antifreeze, proprietary	760	1.
Antiseptic, bathing solution (restricted). ..	220	46.
Antiseptic solutions, U.S.P. or N.F.	244	37, 38-B, 38-F.
Bath preparations	142	1, 3-A, 3-B, 23-A, 30, 36, 38-B, 39-B, 39-C, 40, 40-A.
Bay rum	112	23-A, 37, 38-B, 39, 39-B, 39-D, 40, 40-A.
Biocides, miscellaneous	410	1, 3-A, 3-B, 23-A, 23-H, 27-A, 27-B, 30, 37, 38-B, 39-B, 40, 40-A.
Blood and blood products (processing). ..	345	1, 3-A, 12-A, 13-A, 23-A, 30.
Brake fluids	720	1, 3-A.
Candy glazes	015	13-A, 23-A, 35, 35-A, 45.
Cellulose coatings	011	1, 23-A.
Cellulose compounds (dehydration). ..	311	1, 2-B, 3-A, 32.
Cellulose intermediates	034	1, 3-A, 13-A, 19, 23-A, 32.
Chemicals (miscellaneous)	579	1, 2-B, 2-C, 3-A, 6-B, 12-A, 13-A, 17, 20, 29, 30, 32, 36.
Cleaning solutions	450	1, 3-A, 23-A, 23-H, 30, 36, 39-B, 40.
Coatings, miscellaneous	016	1, 27-A.

Table VII (continued)
AUTHORIZED USES OF
SPECIALLY DENATURED ALCOHOL¹

Product or process	Code No.	Formulas authorized
Collodions, industrial	034	1, 3-A, 13-A, 19, 23-A, 32.
Collodions, U.S.P. or N.F.	241	13-A, 19, 32.
Colognes	122	38-B, 39, 39-A, 39-B, 39-C, 40, 40-A.
Crude drugs (processing)	341	1, 2-B, 3-A, 23-A, 30.
Cutting oils	730	1, 3-A.
Dehydration products, miscellaneous	315	1, 2-B, 3-A.
Dentifrices	131	31-A, 37, 38-B, 38-C, 38-D.
Deodorants (body)	114	23-A, 38-B, 39-B, 39-C, 40, 40-A.
Detergents, household	450	1, 3-A, 23-A, 23-H, 30, 36, 39-B, 40.
Detergents, industrial	440	1, 3-A, 23-A, 30.
Detonators	574	1, 6-B.
Disinfectants	410	1, 3-A, 3-B, 23-A, 23-H, 27-A, 27-B, 30, 37, 38-B, 39-B, 40, 40-A.
Drugs and medicinal chemicals.	575	1, 2-B, 2-C, 3-A, 6-B, 12-A, 13-A, 17, 29, 30, 32.
Drugs, miscellaneous (processing)	349	1, 2-B, 3-A, 13-A, 23-A, 30, 35-A, 38-B.
Duplicating fluids	485	1, 3-A, 30.
Dyes and intermediates	540	1, 2-B, 2-C, 3-A, 12-A, 29, 36.
Dyes and intermediates (processing)	351	1, 2-B, 3-A, 12-A.
Dye solutions, miscellaneous	482	1, 3-A, 23-A, 30, 39-C, 40.
Embalming fluids, etc.	420	1, 3-A, 22, 23-A.
Esters, ethyl (miscellaneous)	523	1, 2-B, 2-C, 3-A, 6-B, 12-A, 13-A, 17, 29, 32, 35-A.
Ether, ethyl	561	1, 2-B, 13-A, 29, 32.
Ethers, miscellaneous	562	1, 2-B, 13-A, 29, 32.
Ethyl acetate	521	1, 2-B, 29, 35-A.
Ethylamines (rubber processing)	530	1, 2-B, 2-C, 3-A, 12-A, 29, 36.
Ethyl chloride	522	1, 2-B, 29, 32.
Ethylene dibromide	571	1, 2-B, 29, 32.
Ethylene gas	572	1, 2-B, 29, 32.
Explosives	033	1, 2-B, 3-A.
External pharmaceuticals (not U.S.P. or N.F.)	210	23-A, 23-F, 23-H, 27-A, 27-B, 36, 37, 38-B, 38-F, 39-B, 40, 40-A.
External pharmaceuticals, miscellaneous (U.S.P. or N.F.)	249	23-A, 25, 25-A, 38-B.
Fluid uses, miscellaneous	750	1, 3-A, 23-A, 30.
Food products, miscellaneous (processing)	332	1, 2-B, 3-A, 13-A, 23-A, 30, 32, 35-A.
Fuel uses, miscellaneous	630	1, 3-A, 28-A.
Fuels, airplane and supplementary	612	1, 3-A, 28-A.
Fuels, automobile and supplementary	611	1, 3-A, 28-A.
Fuels, proprietary heating	620	1, 3-A, 28-A.
Fuels, rocket and jet	613	1, 3-A, 28-A.
Fungicides	410	1, 3-A, 3-B, 23-A, 23-H, 27-A, 27-B, 30, 37, 38-B, 39-B, 40, 40-A.
Glandular products (processing)	342	1, 2-B, 3-A, 12-A, 13-A, 23-A, 30, 32, 35-A.
Hair and scalp preparations	111	3-B, 23-A, 23-F, 23-H, 37, 38-B, 39, 39-A, 39-B, 39-C, 39-D, 40, 40-A.
Hormones (processing)	342	1, 2-B, 3-A, 12-A, 13-A, 23-A, 30, 32, 35-A.
Incense	470	3-A, 22, 37, 38-B, 39-B, 39-C, 40, 40-A.
Inks	052	1, 3-A, 13-A, 23-A, 30, 32, 33.
Insecticides	410	1, 3-A, 3-B, 23-A, 23-H, 27-A, 27-B, 30, 37, 38-B, 39-B, 40, 40-A.
Iodine solutions (including U.S.P. and N.F. tinctures)	230	25, 25-A.
Laboratory reagents (for sale)	810	3-A, 30.
Laboratory uses ²	810	3-A, 30.
Lacquer thinners	042	1, 23-A.
Liniments (U.S.P. or N.F.)	243	27, 27-B, 38-B.
Lotions and creams (body, face, and hand)	113	23-A, 23-H, 31-A, 37, 38-B, 39, 39-B, 39-C, 40, 40-A.
Medicinal chemicals (processing)	344	1, 2-B, 2-C, 3-A, 12-A, 13-A, 17, 23-A, 30, 32, 35-A.

Table VII (continued) **AUTHORIZED USES OF** **SPECIALLY DENATURED ALCOHOL¹**

Product or process	Code No.	Formulas authorized
Miscellaneous chemicals (processing).	358	1, 2-B, 2-C, 3-A, 12-A, 13-A, 17, 23-A, 30, 35-A.
Miscellaneous products (processing)	359	1, 2-B, 2-C, 3-A, 12-A, 13-A, 17, 23-A, 30, 35-A.
Mouth washes	132	37, 38-B, 38-C, 38-D, 38-F.
Organo-silicone products	576	2-B, 3-A.
Pectin (processing)	331	1, 2-B, 3-A, 13-A, 23-A, 30, 35-A.
Perfume materials (processing)	352	1, 2-B, 3-A, 12-A, 13-A, 30.
Perfumes and perfume tinctures	121	38-B, 39, 39-B, 39-C, 40, 40-A.
Petroleum products	320	1, 2-B, 3-A.
Photoengraving dyes and solutions	481	1, 3-A, 13-A, 30, 32.
Photographic chemicals (processing)	353	1, 2-B, 3-A, 13-A, 30.
Photographic film and emulsions	031	1, 2-B, 3-A, 13-A, 19, 30, 32.
Pill and tablet manufacture	349	1, 2-B, 3-A, 13-A, 23-A, 30, 35-A, 38-B.
Plastics, cellulose	021	1, 2-B, 3-A, 12-A, 13-A, 30.
Plastics, non-cellulose (including resins)	022	1, 2-B, 3-A, 12-A, 13-A, 30.
Polishes	051	1, 3-A, 30, 40.
Preserving solutions	430	1, 3-A, 12-A, 13-A, 22, 23-A, 30, 32, 37, 38-B, 42, 44.
Proprietary solvents (standard formulas)	041	1.
Refrigerating uses	740	1, 3-A, 23-A, 30.
Resin coatings, natural	014	1, 23-A.
Resin coatings, synthetic	012	1, 23-A.
Room deodorants	470	3-A, 22, 37, 38-B, 39-B, 39-C, 40, 40-A.
Rosin (processing)	354	1, 3-A, 12-A.
Rotogravure dyes and solutions	481	1, 3-A, 13-A, 30, 32.
Rubber (latex) (processing)	355	1, 3-A.
Rubber, synthetic	580	29, 32.
Rubbing alcohol compound	220	23-H.
Scientific instruments	710	1, 3-A.
Shampoos	141	1, 3-A, 3-B, 23-A, 27-B, 31-A, 36, 38-B, 39-A, 39-B, 40, 40-A.
Shellac coatings	013	1, 23-A.
Soaps, industrial	440	1, 3-A, 23-A, 30.
Soaps, toilet	142	1, 3-A, 3-B, 23-A, 30, 36, 38-B, 39-B, 39-C, 40, 40-A.
Sodium ethylate, anhydrous (restricted)	524	2-B, 2-C.
Sodium hydrosulfite (dehydration)	312	1, 2-B, 3-A.
Soldering flux	035	1, 3-A, 23-A, 30.
Solutions, miscellaneous	485	1, 3-A, 23-A, 30, 39-B, 40, 40-A.
Solvents and thinners, miscellaneous	042	1, 23-A.
Solvents, special (restricted sale)	043	1.
Stains (wood)	053	1, 3-A, 23-A, 30.
Sterilizing solutions	430	1, 3-A, 12-A, 13-A, 22, 23-A, 30, 32, 37, 38-B, 42, 44.
Theater sprays	470	3-A, 22, 37, 38-B, 39-B, 39-C, 40, 40-A.
Tobacco sprays and flavors	460	4.
Toilet waters	122	38-B, 39, 39-A, 39-B, 39-C, 40, 40-A.
Transparent sheetings	032	1, 2-B, 3-A, 13-A, 23-A.
Unclassified uses ³	900	1, 3-A.
Vaccine (processing)	343	1, 2-B, 3-A, 12-A, 13-A, 23-A, 30, 32, 35-A.
Vinegar	511	18, 35-A.
Vitamins (processing)	342	1, 2-B, 3-A, 12-A, 13-A, 23-A, 30, 32, 35-A.
Xanthates	573	1, 2-B, 2-C, 29.
Yeast (processing)	342	1, 2-B, 3-A, 12-A, 13-A, 23-A, 30, 32, 35-A.

¹ Other products or processes may be authorized by the Director under §212.15(b).

² Formula No. 3-A and Formula No. 30 are authorized for general laboratory purposes under Code 810. Other formulas may be authorized for laboratory use in connection with specific product development.

³ Persons desiring other formulas for this use should indicate the fact in the space provided for this purpose on Form 1479-A.

Proprietary Solvents

Proprietary solvents may be purchased without a permit or bond by any person for use in manufacturing or as a solvent. These solvents are made with specially denatured alcohol according to formulas authorized by Federal regulations. All are based on S.D.A. No. 1 and by law must contain more than 25% alcohol by volume. Table VIII lists the five authorized proprietary solvent formulations.

Table VIII
AUTHORIZED PROPRIETARY SOLVENT
FORMULATIONS
(309)

	Formulation (in gallons)				
	No. I	No. II	No. III	No. IV	No. V
S.D.A. No. 1	100	100	100	100	100
Ethyl Acetate	5	1	1	—	—
Gasoline	1	1	1	1	1
Denaturing Grade Wood Alcohol	—	2	—	—	—
Methyl Isobutyl Ketone	—	—	1	1	1
tert-Butyl Alcohol	—	—	—	2	—
sec-Butyl Alcohol	—	—	—	—	2

JAYSOL, the Enjay Chemical Company's proprietary solvent, is based on Formulation III in Table VIII. It is available in 190 proof and anhydrous grades. Typical inspections for JAYSOL are shown in Table IX.

Proprietary solvents are relatively mild-odored and are widely used in industry, as well as in the home and workshop. In the fiscal year ending June 30, 1960, over 21 million wine gallons of specially denatured alcohol went into proprietary solvents. Shellac, nitro-cellulose lacquers, varnishes, cleaning solutions, fuels and adhesives are only a few of the uses for these versatile solvents.

Table IX
TYPICAL INSPECTIONS FOR JAYSOL
PROPRIETARY SOLVENT

Composition: One hundred gallons of S.D.A. No. 1, one gallon of methyl isobutyl ketone, one gallon of ethyl acetate, and one gallon of gasoline (unleaded).

	190 Proof Formulation	200 Proof Formulation
Apparent Proof (60/60°F)	190.6	199.4
Specific Gravity (60/60°F)	0.8155	0.7955
Pounds Per Gallon (60°F)	6.79	6.62
Acidity, as acetic acid (wt %)	<0.001	<0.001
Color (Pt-Co)	<5	<5
Non-volatile Matter (mg/100 ml)	<1	<1
Appearance	Clear and Free of Suspended Matter	Clear and Free of Suspended Matter
Flash Point, $\pm 5^{\circ}\text{F}$ (Tag. Open Cup)	45	43

Special Industrial Solvents

Special industrial solvents are used in industrial applications which cannot tolerate the presence of hydrocarbon denaturants. These solvents can be purchased without a permit or bond, however, only legitimate industrial users can obtain them. Retail distribution of special industrial solvents is prohibited.

JAYSOL-S is the Enjay Chemical Company's special industrial solvent. It is made in accordance with Formulation A of Table X, which lists the three government-authorized formulations, all based on S.D.A. No. 1. Table XI gives typical inspections for JAYSOL-S.

Special industrial solvents were largely developed for the printing industry. The rubber rolls and plates used in offset printing can be cleaned with these solvents without danger of softening. Offset printing inks are often formulated with special industrial solvents. These solvents are completely miscible with water and do not cloud up when used on rotogravure equipment. Some other uses are in drying photographic film, textile and shoe dyeing, zinc etching and film packaging.

Table X
AUTHORIZED SPECIAL INDUSTRIAL SOLVENT
FORMULATIONS
(309)

	Formulation (in gallons)		
	A	B	C
S.D.A. No. 1	100	100	100
Isopropyl Alcohol	10	5	—
Methyl Isobutyl Ketone	1	1	1
Methyl Alcohol	—	5	—
Ethyl Acetate	—	—	5

Table XI
TYPICAL INSPECTIONS FOR JAYSOL-S
SPECIAL INDUSTRIAL SOLVENT

Composition: One hundred gallons of S.D.A. No. 1, ten gallons of isopropyl alcohol (anhydrous), and one gallon of methyl isobutyl ketone.

	190 Proof Formulation	200 Proof Formulation
Apparent Proof (60/60°F)	191.5	199.5
Specific Gravity (60/60°F)	0.8128	0.7948
Pounds Per Gallon (60°F)	6.77	6.62
Acidity, as acetic acid (wt %)	<0.001	<0.001
Color (Pt-Co)	<5	<5
Non-volatile Matter (mg/100 ml) . . .	<1	<1
Appearance	Clear and Free of Suspended Matter	Clear and Free of Suspended Matter
Flash Point, $\pm 5^{\circ}\text{F}$ (Tag. Open Cup) . .	62	60

Completely Denatured Alcohol (C.D.A.)

Completely denatured alcohol is tax-free and can be bought and used with a minimum of restriction. No permit or bond is needed. The denaturants present in completely denatured alcohol make it unfit for human consumption. Two formulas are authorized for completely denatured alcohol, although in recent years only C.D.A. 19



has been of commercial importance. In fiscal year 1961, only 819,634 wine gallons were produced.

C.D.A. Formula No. 19 consists of 100 gallons of ethyl alcohol of not less than 160 proof, 4.0 gallons of methyl isobutyl ketone, and 1.0 gallon of kerosene.

The odor of completely denatured alcohol is not as mild as that of specially denatured alcohol or proprietary solvents. Also, the kerosene present cannot be tolerated in many products and processes that employ ethyl alcohol. These factors, plus its replacement by other fluids as an antifreeze, have contributed to completely denatured alcohol's decreasing importance. Some current uses are in the manufacture of cleaning fluids, surface coatings and fuels.

Pure Industrial Alcohol

There are a number of applications for which pure (undenatured) ethyl alcohol is needed. Table XII gives typical inspections for 190 proof and 200 proof pure alcohol. Both grades are commercially available on either a tax-paid or tax-free basis.

Table XII
TYPICAL INSPECTIONS FOR PURE INDUSTRIAL
ETHYL ALCOHOL

	190 Proof	200 Proof
Purity (vol %)	95.1	99.9+
Specific Gravity (60/60°F)	0.815	0.793
Pounds Per Gallon (60°F)	6.79	6.61
Acidity, as acetic acid (wt %)	<0.001	<0.001
Color (Pt-Co)	<5	<5
Non-volatile Matter (mg/100 ml)	<1.0	<1.0
Distillation (°C)		
Initial	78.0	78.2
Dry Point	78.4	78.4
Permanganate Time (minutes)	60	45
Residual Odor	Nil	Nil
Water Solubility	Clear at Infinite Dilution	Clear at Infinite Dilution
Appearance	Clear and Free of Suspended Matter	Clear and Free of Suspended Matter
Flash Point, $\pm 5^{\circ}\text{F}$ (Tag. Open Cup)	68	65

TAX-PAID

Pure ethyl alcohol can be released from Federal bond by payment of the Federal tax of \$10.50 per proof gallon. Manufacturers and others who wish to obtain pure ethyl alcohol for non-beverage use do not need a permit or bond to purchase it (313).

Federal law provides for a drawback (refund) of taxes upon tax-paid alcohol used in the manufacture of medicines, medicinal preparations, food products, flavors, or flavoring extracts, which are unfit for beverage purposes (314). This drawback is equal to \$9.50 per proof gallon for domestic products and \$10.50 per proof gallon for exported products.

TAX-FREE

Pure ethyl alcohol may be withdrawn free of tax by and for the following (310):

- (1) the United States or any governmental agency thereof;
- (2) any State, any political subdivision thereof, or the District of Columbia;
- (3) any educational organization which is exempt from income tax, or any scientific university or college of learning;
- (4) any laboratory for use exclusively in scientific research;
- (5) any hospital, blood bank, sanatorium, or any pathological laboratory exclusively engaged in making tests for hospitals or sanitoriums; and
- (6) any clinic operated for charity and not for profit.

Tax-free alcohol may only be used for non-beverage purposes. It cannot be resold or used in the manufacture of any product for sale. All eligible users must obtain a permit in order to buy and use tax-free alcohol.

CHEMICAL PROPERTIES AND APPLICATIONS

Ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) is a primary alcohol and undergoes reactions typical of alcohols of this type; thus, its chemistry is primarily that of the hydroxyl group. The hydrogen atom of this group may be replaced by metals to form ethoxides (ethylates). The opening of epoxide rings to form hydroxy ethyl ethers and the addition of ethyl alcohol to acetylene also involves this hydrogen atom. The hydroxyl group can be replaced by halogens from hydrogen halides and phosphorus halides. Esters are formed by the reaction with both inorganic and organic acids.

Ethyl alcohol can be dehydrated to ethylene or ethyl ether by various reagents including sulfuric acid and aluminum oxide. Oxidation and dehydrogenation of ethyl alcohol both produce acetaldehyde which upon further oxidation yields acetic acid. The production of acetaldehyde is the largest use of ethyl alcohol.

The methyl group of ethyl alcohol plays a role in a number of reactions including dehydration to ethylene and oxidation by halogens. The acetaldehyde produced by halogen oxidation is further halogenated to the trihaloacetal. The trihaloacetal will react with a strong base to produce haloform (CHX_3) and the metal formate.

Bobtelsky has proposed that ethyl alcohol-water mixtures may be divided into three distinct "zones" in respect to alcohol content (315). The low zone has 25-30% alcohol, the middle zone 40-60% ethyl alcohol and the high zone contains more than 60% alcohol. The chemical reactions in each of these zones proceed in a well-defined way characteristic for the particular zone. The chromium trioxide oxidation of ethyl alcohol (316), the catalytic decomposition of hydrogen peroxide (317) and the sensitivity of colloidal particles to coagulation (318) are examples of reactions which are markedly influenced by the ethyl alcohol content of the reaction mixture.

In the oxidation of ethyl alcohol by chromium trioxide there occurs a "low," "middle," and "high" zone of activity in the presence of fixed amounts of various mixed acids. In the "low" zone, the rate of oxidation is proportional to the concentration of the alcohol; in the "middle" zone (3-8 moles of water per mole of ethyl alcohol), the

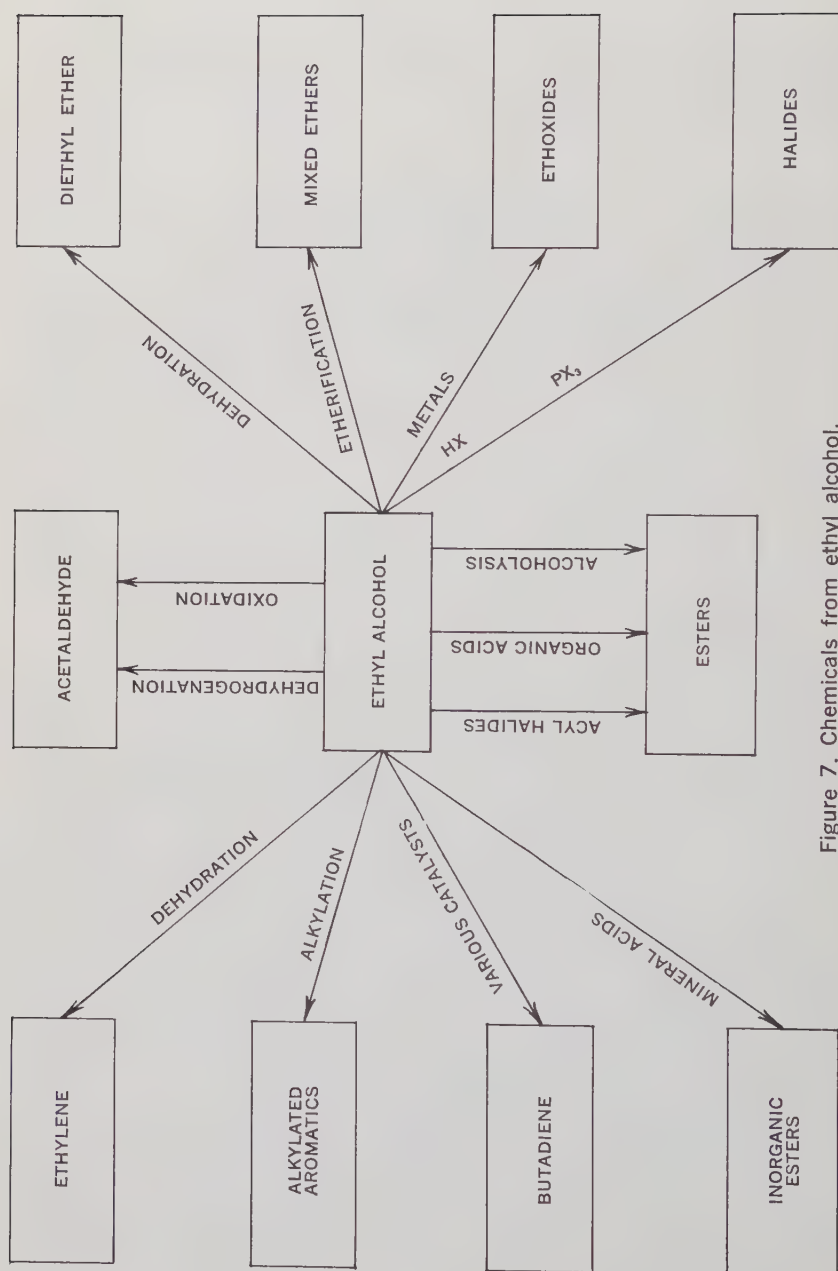


Figure 7. Chemicals from ethyl alcohol.

velocity falls very slightly with increasing concentration of the ethyl alcohol; and in the "high" zone (above 60% ethyl alcohol), the velocity increases very sharply. The temperature coefficients differ greatly but vary in a regular way in the "low" and "high" zones, but in the "medium" zone they show no regularities. The influence of various acids and catalysts also are different for different alcohol concentrations. The catalytic decomposition of hydrogen peroxide is retarded by small amounts of ethyl alcohol (up to 5%) in the presence of specific catalysts, but concentrations from 5-30% materially increase the rate of decomposition. Between 30% and 60%, the catalyzed reaction shows a steady maximum; above 60% it stops. These observations are explained by the strong hydrogen bond between alcohol molecules and water molecules (315). The arrangement of the molecules in the mixed solvent is dependent upon their relative amounts in the mixture.

Typical reactions of ethyl alcohol are given in Figure 7.

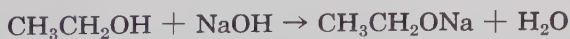
Table XIII lists the quantities of ethyl alcohol used as a raw material in the production of various chemicals during the fiscal year ended June 30, 1960. The use of ethyl alcohol by the chemical industry has been the subject of several review articles of which the following are typical: Martraire (1944) (319), Weizmann, Bergmann and Sulzbacher (1947) (320), Guinot (1946, 1953) (321, 322) and Anonymous (1955) (323).

Reaction with Metals

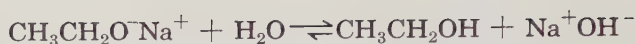
Absolute alcohol (ethanol) reacts readily with active metals such as sodium and potassium to form the metal ethoxide (ethylate, alcoholate) and hydrogen.



Sodium ethoxide may be prepared by the reaction between absolute alcohol and sodium and by refluxing absolute alcohol in the presence of anhydrous sodium hydroxide (324).



The sodium ethoxide will precipitate upon the addition of anhydrous acetone (326). It is a strong base and hydrolyzes almost completely in water to yield ethyl alcohol and sodium and hydroxyl ions.



This is an equilibrium reaction and removal of the water by azeotropic distillation with benzene is used commercially as a process for sodium ethoxide production (327). The reaction between sodium amalgam and alcohol is another possible source of sodium ethoxide.

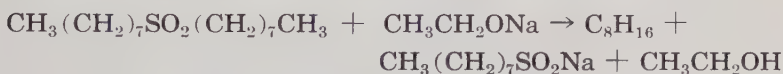
Table XIII
USES OF SPECIALLY DENATURED ALCOHOL AS A
CHEMICAL RAW MATERIAL DURING FISCAL YEAR
ENDED JUNE 30, 1960
(325)

Quantities In Wine Gallons			
Product or Use	New Alcohol used ¹	Recovered Alcohol Used ²	Alcohol Recovered For Use
USED AS A RAW MATERIAL IN PRODUCTION OF OTHER CHEMICALS:			
Vinegar	10,993,806	—	—
Acetic acid	4,379,215	—	—
Ethyl acetate	6,907,112	1,166,904	1,015,849
Ethyl chloride	6,337,061	—	—
Other ethyl esters	8,925,825	2,475,995	1,881,062
Dyes and intermediates	160,506	105,881	38,267
Aldehydes	156,335,992	1,152,670	1,140,572
Ether, ethyl	647,151	—	—
Ethers, glycol and ethers other than ethyl	8,474,013	52,165,816	52,345,381
Ethylene dibromide	125,112	—	—
Ethylene gas	178,362	—	—
Xanthates	210,334	—	—
Fulminate of mercury	594	—	—
Drugs and medicinal chemicals	779,946	4,881,951	4,905,150
Organo-silicone products	128,782	—	—
Miscellaneous	7,061,745	24,653	3,226,794
Synthetic resins	—	20,667,545	17,454,538
Synthetic rubber	14	—	—
Rubber accelerators	1,828,224	—	—
Total	213,473,794	82,641,415	82,007,613

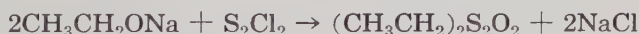
¹ Represents quantity of alcohol used for the first time, whether or not any quantity is subsequently recovered.

² Represents quantity of alcohol reused after recovery from processes where the alcohol has not become a part of the finished products. Such alcohol may have been recovered during the fiscal year 1960 or prior thereto and from any of the listed processes.

Sodium ethoxide is an important condensing agent and catalyst in organic synthesis. Simultaneous hydrogenation of unsaturated triglycerides and interesterification with other esters (tributyryn or ethyl butyrate) have been carried out in the presence of nickel hydrogenation catalyst and sodium ethoxide (328). Sodium ethoxide has also been used to catalyze the alkylation of fluorene with ethyl alcohol (329). The reduction of tetracyclone 2,4-dinitrophenylhydrazone to 1-ethyl-2,3,4,5-tetraphenylcyclopentadiene can be effected by ethanolic sodium ethoxide (330). Vitamin K (and other 2,3-dialkylated 1,4-naphthoquinones) can be assayed by the addition of a solution of sodium N,N-diethyldithiocarbamate and sodium ethoxide followed by measurement of the resulting deep blue color (331). Sulfones may be cleaved by alcoholic sodium ethoxide (332).

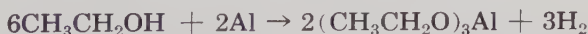


The action of sulfur monochloride on sodium ethoxide yields diethyl thiosulfite (333).



Sodium ethoxide is used commercially in the production of barbital (Veronal, Barbital, Luminal, Amytal), ethyl ortho carbonate and other chemicals.

Aluminum ethoxide may be prepared by several processes based on the reaction of the metal with absolute alcohol.



Well-cleaned aluminum filings will react at room temperature in the presence of catalytic amounts of mercuric chloride (334, 335).

Metallic aluminum and ethanol will react without a catalyst at 120°C in an autoclave (336). Sodium ethoxide has been patented as an additive to the reaction mixture to promote the reaction (337).

Reaction with Inorganic Acids

Ethyl alcohol will react with the common inorganic acids to form esters. If the acid is oxygenated (H_2SO_4 , HNO_3) the ester will have a carbon-oxygen-heteroatom linkage and be easily hydrolyzed.



The halogen acids also produce esters but of a more stable type ($\text{CH}_3\text{CH}_2\text{X}$) and generally they are not classified as esters, but as alkyl halides.



The order of reactivity is $\text{HI} > \text{HBr} > \text{HCl}$.

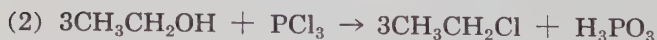
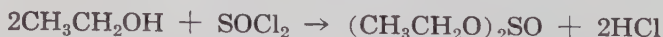
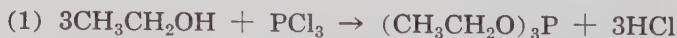
Both of these are equilibrium reactions and appreciable study has gone into devising methods for forcing the reaction to the right. The study with the halogen acids has centered on hydrogen chloride and hydrochloric acid because of the economic position of ethyl chloride. The two most important uses of ethyl chloride are to make tetraethyl lead and ethyl cellulose. Vapor phase processes usually consist of passing ethyl alcohol and hydrogen chloride over a contact catalyst at a high temperature (338). A temperature of $240\text{--}300^\circ\text{C}$ with activated carbon impregnated with phosphoric acid is typical.

Ethyl chloride is produced commercially by the aluminum chloride catalyzed reaction between ethylene and hydrogen chloride in ethylene dichloride.

Ethyl chloride has also been produced commercially by the liquid phase reaction between ethyl alcohol and hydrochloric acid in a 45% zinc chloride solution at 145°C (339). This is a continuous process with yields of 95 to 98% based on the ethyl alcohol. Other catalysts such as bismuth chloride (340) have been proposed.

Ethyl bromide is readily prepared by the reaction between ethyl alcohol and hydrogen bromide generated by the action of sulfuric acid on sodium bromide. The addition of metallic copper is said to increase the yield from 57% to 80% (341). Apparently the copper prevents oxidation of the bromide ion to bromine. Ethyl bromide may be used to produce ethyl Grignard reagent and various amines including mono- and diethyl aniline.

The reaction between inorganic acid halides (PX_3 , SOCl_2) and ethyl alcohol may give two different products: (1) the ethyl ester of the acid and (2) the ethyl halide.



With phosphorus trichloride the predominant product is triethyl phosphite but with phosphorus tribromide the product is predominantly ethyl bromide. Diethyl hydrogen phosphite can be produced by modifications of the reaction with phosphorus trichloride (342). Thionyl chloride gives diethyl sulfite as the main product. The iodide may be prepared by the reaction between ethyl alcohol, red phosphorus and iodine.

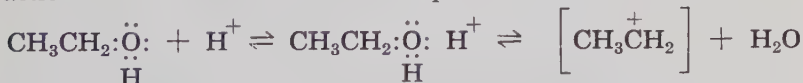
The reaction between sulfuric acid and ethyl alcohol will yield several different products depending upon acid concentration, temperature and other variables. The slow addition of sulfuric acid to ethyl alcohol will produce *ethyl hydrogen sulfate*.



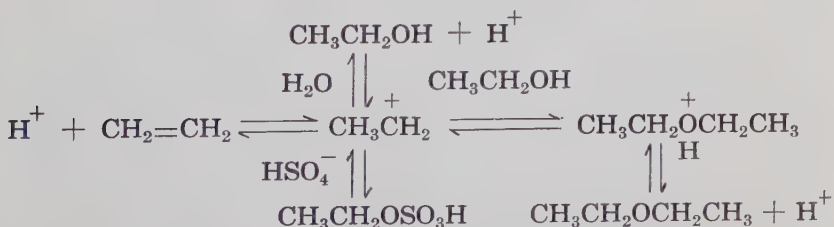
This solution, on slow vacuum distillation, yields *diethyl sulfate*. Diethyl sulfate is a powerful ethylating agent.

The equilibrium involved in the production of the ethyl hydrogen sulfate has been studied by Suter and Oberg (343). They obtained the following equilibrium constants with 96.7% sulfuric acid: 25°C, $K=1.76$; 35°C, $K=1.84$. The activity of ethyl alcohol in dilute sulfuric acid was reported by Gallagher and Keyes (344). The activity was obtained from the partial pressures of the ethyl alcohol over the dilute acid.

The sulfuric acid catalyzed dehydration of ethyl alcohol can lead to ethylene or ethyl ether, depending upon the temperature of the reaction mixture. The initial reaction produces a carbonium ion.



The carbonium ion may react in four different ways.



The presence of water (dilute acid) will give essentially no reaction (all alcohol). High temperatures (150-160°C) and an excess

of acid favors the formation of ethylene and ethyl hydrogen sulfate while good yields of ethyl ether are obtained with an excess of ethyl alcohol and a temperature range of 127-140°C.

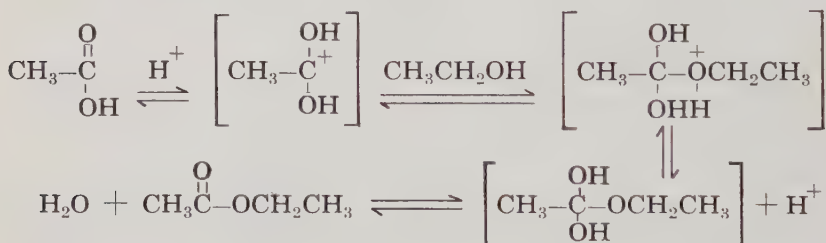
Ethyl nitrite ($\text{CH}_3\text{CH}_2\text{ONO}$) can be produced in a vapor phase reaction with nitrogen dioxide in the presence of a diluent (345).

Esterification of Carboxylic Acids

One of the most useful chemical reactions of ethyl alcohol is its reaction with an organic acid to form an ester.



This is a hydrogen ion catalyzed reaction and it is thought to involve the following sequence of reactions.



A proton from the acid catalyst adds to the electron-rich oxygen atom of the carboxyl group to form a carbonium ion. This ion adds a molecule of ethyl alcohol to produce an unstable intermediate that loses water and a proton. All the steps are reversible and an equilibrium is established. A few organic acids are sufficiently ionized to be self-catalyzing for their esterification but catalytic amounts of a strong acid (sulfuric acid) are usually added. Hydrochloric acid, boron trifluoride (346) and *p*-toluenesulfonic acid are also used as esterification catalysts.

The technology of esterification with ethyl alcohol is mainly concerned with removal of the water produced by the reaction to shift the equilibrium to the right. Excellent yields of esters can be obtained from a variety of acids by proper choice of apparatus and reaction conditions.

Ethyl acetate production represents not only a typical esterification process but also the most important esterification reaction of ethyl alcohol.



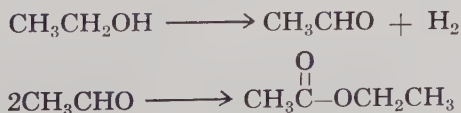
The reaction reaches an equilibrium with about 67% conversion to ethyl acetate when equal molar quantities of acetic acid and ethyl alcohol are used (347). In order to obtain a higher yield of ester the reaction is forced to the right by using an excess of ethyl alcohol and by removal of the water formed. The esterification may be either a batch or continuous process depending upon the concentration of the acetic acid and the size of the operation. Sulfuric acid is used as the catalyst. The acetic acid concentration will vary from 8% to about 80% but 95% ethyl alcohol is generally used and 50 to 66° Bé sulfuric acid. The ratio of reactants will vary depending upon the process and type of equipment. A batch process may use the following proportions by weight:

Acetic acid (8%)	10 parts
Ethyl alcohol (95%)	10 parts
Sulfuric acid (66°Bé)	0.33 part

The continuous process uses an esterification column the head of which is held at 80°C. The distillate from this column contains about 70% alcohol, 20% ester and 10% water. This mixture is concentrated by azeotropic distillation to its ternary (82.6% ethyl acetate, 8.4% ethyl alcohol, 9.0% water) which is further treated to give 95 to 99% ethyl acetate. The yield of ethyl acetate is 99 to 100% based on acetic acid. The batch process gives a yield of about 95%.

Acetic acid can be esterified directly with ethyl alcohol in the vapor phase by adsorption of the acetic acid on a solid catalyst (348, 349). The adsorption of the acetic acid is rate controlling.

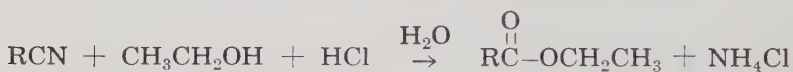
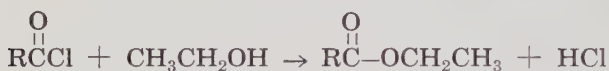
The formation of ethyl acetate by direct conversion of ethyl alcohol has been studied. Ivannikov and Gavrilova obtained a 24% yield of ethyl acetate using a copper oxide catalyst containing 0.1-0.2% thoria and a temperature of 350°C (350). A more extensive study of this type of reaction was made by Dolgov and his co-workers (351) and its industrial implications were evaluated by Beizel, Hel'ms and Le'l'chuk (352). The reaction is thought to go by way of acetaldehyde and its condensation to ethyl acetate (the *Tishchenko Reaction*).



Acetaldehyde is one of the products of the direct conversion of ethyl alcohol to ethyl acetate by this procedure. Modification of the catalyst and a change in temperature will cause the product to be predominantly either ethyl acetate or *n*-butyl alcohol (353, 354).

Terephthalic acid can be esterified by both methyl and ethyl alcohol in a noncatalytic process by carrying out the reaction above the critical temperature of the alcohol and in the presence of added diester of terephthalic acid (355).

Various acid derivatives may be used to produce the ethyl ester of the parent acid. These include acid chlorides, anhydrides and nitriles.



James and Bryan (356) report that the use of aromatic sulfonic acids (*p*-toluenesulfonic acid) as a catalyst for the alcoholysis of nitriles to esters will avoid the corrosion and charring which sometimes accompanies the use of hydrochloric (357) or sulfuric acid (358, 359). Diethyl malonate is produced commercially from cyanoacetic acid by alcoholysis and esterification in the presence of concentrated sulfuric acid (360).

Physical properties of various organic esters are given in Table XIV.

Ethyl acetate is used extensively as a nitrocellulose lacquer solvent and in general solvent applications for inks, nail enamels, photographic films, smokeless powder, plastic wood, thinners, dopes, and varnishes. It is a solvent in the purification of antibiotics, and an extractant in the concentration of dilute solutions of acetic acid. It is widely used in synthesis (ethyl acetoacetate, acetamide, acetyl ethylamide, others) but this use represents only a small percentage of its total production.

Ethyl formate is an effective fumigant against raisin moth, dried fruit beetle, fig moth, Indian meal moth and the confused flour beetle. Both ethyl acetate and ethyl formate are used in synthetic flavors. Ethyl formate is an ingredient in artificial rum and arrack and in lemon and strawberry flavors. It is also used in *Claisen condensations*

Table XIV
PHYSICAL PROPERTIES OF ORGANIC ESTERS OF
ETHYL ALCOHOL

Ester	Boiling Point, °C	Freezing Point, °C	Specific Gravity ²⁰ ₄	Index of refraction, n ²⁰ _D
Formate	54.15	— 79.4	0.9226	1.35975
Acetate	77.15	— 83.6	0.90056	1.37243
Propionate	99.10	— 73.85	0.89017	1.38395
n-Butyrate	121.5	—100.8	0.87917	1.3928
iso-Butyrate . . .	110.1	—	0.86930	1.3903
n-Valerate	146	—	0.8739	1.40094
iso-Valerate . . .	135	—	0.8657	1.39671 (18.3°)
Trimethylacetate	118.35	— 89.55	0.85467	1.39061
Caproate	167.85	— 67.6	0.87121	1.40758
Heptanoate	188.55	— 66.3	0.86856	1.41296
Caprylate	208.5	— 43.2 (α)	0.86651	1.41775
Nonanoate	227.0	— 55.0 (α)	0.86511	1.42200
Caprate	244.9	— 18.0 (α)	0.86407	1.42575
Laurate	269	—	0.8616	1.4321
Myristate	295	+ 11.93	0.8589	—
Stearate	—	+ 33.8	—	—
Oxalate	185.65	— 40.6	1.0785	1.41011
Malonate	199.35	— 51.5	1.0550	1.41618
Succinate	217.75	— 21.3	1.0402	1.42010
Glutarate	233.68	— 23.80	1.02206	1.42400
Adipate	240	— 19.8	1.00693	—

and it can be used in the synthesis of sulfadiazine and sulfamerazine. Ethyl esters of higher molecular weight acids may be used as solvents and flavoring materials (Table XV). Ethyl benzoate is used in the production of dyestuffs.

The ethyl esters of dicarboxylic acids are useful as plasticizers and as intermediates for mordants and heat- and light-stable pigments

Table XV
ETHYL ESTERS IN VARIOUS ESSENCES

Ethyl Ester	Essence
Formate	Grape, apple, peach, rum
Acetate	Apple
Propionate	Apple
Butyrate	Apple, apricot, peach, pineapple, rose
Isovalerate	Peach
Caproate	Apple
Heptoate	Cognac, wine, grape
Nonylate	Quince, rose

(diethyl succinate). Ethyl oxalate is used to make phenobarbital and dyestuffs. Diethyl phthalate is used as a plasticizer in cellulose acetate formulations for sheeting and molding.

Dehydration

The dehydration of ethyl alcohol by the action of concentrated sulfuric acid was noted in the section on esters of inorganic acids. The commercial dehydration of ethyl alcohol is usually a vapor phase process using a solid catalyst. The product will be either ethylene or ethyl ether depending on operating conditions and catalyst. During World War II there was extensive development of the catalytic dehydration of ethyl alcohol to produce butadiene.

ETHYLENE

The dehydration of ethyl alcohol to ethylene is of limited industrial importance because of the current availability of ethylene from other sources. A small amount of ethylene is produced commercially, however, by passing ethyl alcohol vapor over activated alumina at 340-350°C. The yield for the reaction is about 96%.

The mechanism of this dehydration has been the subject of several papers by Antipina and co-workers (361-363) and a mechanism has been proposed by Topchieva and Yun-Pin (364). A number of papers have been published on aluminum oxide (365-367) and modified

aluminum oxide (368-370) as catalysts. Hafnium and zirconium oxides act as dehydrating catalysts between 360° and 555°C but the reaction is accompanied by appreciable dehydrogenation (371). The use of aluminum oxide mixed with various other metal oxides has been reported by Kosolapov (372).

Hydration catalysts such as phosphoric and sulfuric acids will also serve as dehydration catalysts and copper, silver and aluminum salts are promoters for this reaction.

ETHYL ETHER

Aluminum oxide also may be used to dehydrate ethyl alcohol to ethyl ether (373-376). The maximum yield depends on the type of catalyst used and on the temperature. Pease and Yung determined the equilibrium in the reaction



at 275°C using alumina as a catalyst and at 130°C using a sulfuric acid-alcohol mixture as catalyst (377). The equilibrium constant (K) at 275°C was 0.66 and 8.0 at 130°C. These figures correspond to a maximum possible conversion of alcohol to ether of 62.0% at 275°C and 85.0% at 130°C. The free-energy change in the reaction and the free energy of formation of ether vapor at 25°C are -3,210 cal and -35,900 cal. They also studied the effect of temperature between 200°C and 350°C on the ratio of ethylene to ethyl ether (378). Ether production reached a maximum at 250°C and ethylene formation was negligible below 275°C.

Treatment of silica-alumina catalysts with alkali sharply reduces the yield of ethylene and increases the yield of ether (379, 380). The -ONa group formed on the catalyst as a result of alkali treatment and linked both to the aluminum atom and the silica atom causes the dehydration to ether instead of to ethylene. Other catalysts which have been proposed include copper sulfate, tin chloride, manganous chloride, aluminum chloride, potash, chrome alum and chromium sulfate (381).

Ethyl ether is used as a solvent and reaction medium.

BUTADIENE

The dehydration of ethyl alcohol to butadiene had been investigated by Lebedev (382) prior to World War II. His process was

utilized by the Russians during World War II and consisted of a catalytic vapor phase reaction over a mixed catalyst of alumina and zinc oxide at 400°C and 0.25 atm. The yield of butadiene was about 50%. The Germans dehydrated alcohol by another process using a supported magnesia catalyst promoted with a small amount of cobalt or chromium oxides. A yield of 60% at 270-300°C and atmospheric pressure was reported. An American-developed process depended upon a catalyst containing 59% magnesia, 2% chromic oxide and 39% silica gel used in a one-step process to give a 38% conversion per pass and an over-all yield of 56% at 400-425°C.

Approximately 60% of the butadiene produced in the United States during World War II was obtained by a two-step process utilizing a mixture of 69 wt % ethyl alcohol, 24 wt % acetaldehyde and 7% water at atmospheric pressure over a catalyst containing 2% tantalum oxide and 98% silica gel at 325-350°C (383-386). The conversion per pass was 30-35% and the over-all yield of butadiene was 63%. The feed material was obtained in an initial step by partial dehydrogenation of ethyl alcohol over a standard copper catalyst. A comprehensive article on this process and the catalysts used has been written by Corson *et al.* (387).

Various other catalysts have been investigated. A 76:11:2:11 mixture of MgO:SiO₂:Cr₂O₃:Aluminum silicate hydrate gave a 65-66% yield at 435°C (388). Romanovsky and Jordan proposed the use of a catalyst consisting of 70% MgO, 20% SiO₂ and 10% CaHPO₄ or Ca₃(PO₄)₂ (389). Natta and Rigamonti obtained the best results from catalysts containing silica (dehydrating catalyst) and magnesia (dehydrogenating catalyst) (390). A magnesium oxide catalyst containing 2.5% Cr₂O₃ and 0.5% CoO as promoters is reported to give an improved yield of butadiene (391) and a catalyst containing 55-80% magnesia, 15-40% silica and 5-25% of *normal calcium nickel phosphate* has been patented (392). The preparation of butadiene using a fluidized bed process has been proposed (393).

Production of Acetaldehyde

The production of acetaldehyde is the most important chemical utilization of ethyl alcohol. The conversion can be accomplished by either oxidation or dehydrogenation of the alcohol, or by a combination of these processes.

OXIDATION

A typical process utilizing oxidation consists of passing alcohol vapors and preheated air over a silver gauze catalyst. The proportion of air is adjusted to permit the exothermal heat of oxidation just to exceed the endothermal heat of dehydrogenation. The reaction temperature depends upon this ratio and will vary from 375° to 550°C. The conversion is about 25 to 35% per pass.

Cullis and Newitt have made a detailed study of the gaseous oxidation of ethyl alcohol between 270° and 370°C (394). The kinetics of the liquid phase oxidation of ethyl alcohol have been reported by Klassen and Kirk (395).

DEHYDROGENATION

A chromium-activated copper catalyst is used for the dehydrogenation of ethyl alcohol to acetaldehyde. The temperature range is 260-290°C and the conversion ranges from 30 to 50% per pass (396). The ethyl alcohol equilibrium conversion at 300°C is 55%, at 400°C it is 86% and at 500°C 95% of the ethyl alcohol will be converted.

The influence of the composition of $\text{ZnO-Fe}_2\text{O}_3$ and $\text{ZnO-Cr}_2\text{O}_3$ catalysts on the yield in the dehydrogenation of ethanol and on the electrical conductivity of the catalyst has been reported by Bielanski and co-workers (383, 397). At constant catalyst composition there is a linear dependence of the change in the absolute value of the log of the conductivity on the reaction yield. The relation of the electrical conductivity and reaction yield to the composition of the catalyst is more complex than in the case of the $\text{MgO-Cr}_2\text{O}_3$ system. The dehydrogenation kinetics over a precipitated copper catalyst has been investigated by Balandin and Teteni (398).

The main use for acetaldehyde is its oxidation to acetic acid. It is also used in the production of croton-aldehyde (399), *n*-butyl alcohol, acetic anhydride, 2-ethylhexanol, pentaerythritol, substituted pyridines, chloral and various other organic compounds. Aromatic and aliphatic amines combine with acetaldehyde to form dyestuffs, rubber accelerators, and anti-oxidants. It will condense with phenol or urea to form thermosetting resins which have applications in varnishes and enamel oils. Acetaldehyde polymerizes to paraldehyde which is used as a convenient source of acetaldehyde. Acetaldehyde is too reactive to be used as a solvent.

Distilled Vinegar

Distilled vinegar is produced by the fermentation of distilled ethyl alcohol by *Bacterium aceti*. The traditional basic raw material has been ethyl alcohol of fermentation origin. The supply picture is changing, however, with synthetic alcohol assuming a role of growing importance. There are several reasons for this change—the most important is the stability of synthetic alcohol supply. This alcohol can be used in conventional equipment and it yields a vinegar with fully acceptable aroma and taste (400).

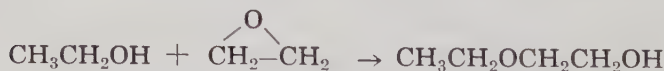
Miscellaneous Reactions

Ethyl alcohol has a number of reactions which are unique besides the usual chemical reactions typical of primary alcohols. In this section the emphasis will be on these unique reactions. The coverage will be illustrative rather than comprehensive.

Chloral was formerly produced by the liquid phase chlorination of ethyl alcohol at reflux temperature in a tower reactor. The temperature was maintained between 78° and 95°C for *ca.* 24 hours. The product was a mixture of chloral hydrate and chloral hemiacetal. This mixture was added to an equal volume of 80-85% sulfuric acid and a mixture of chloral and chloral hydrate was obtained by distillation between 93° and 98°C.

Addition of alkali to chloral cleaves the molecule to chloroform and a formate. These are general reactions for the halides (*haloform reaction*) and may be used for the production of bromoform and iodoform. Chloral is used in the synthesis of DDT.

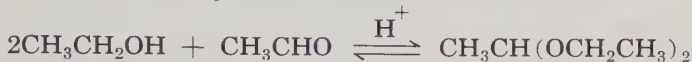
Ethyl alcohol will open an oxide ring to yield an ether alcohol.



The reaction is relatively slow and requires a high temperature (200°C) and high pressures (400-600 psi). Both acids and bases catalyze the reaction but acids are corrosive and bases simultaneously catalyze polymer formation. The reaction is reported to go readily at room temperature in the presence of sodium ethoxide, however, to give an 80% yield of a mixture of mono-, di- and triethylene glycol (401). The monoethyl ether of ethylene glycol is a nitrocellulose

solvent. Diethylene glycol monoethyl ether is produced by the reaction between ethylene glycol monoethyl ether and ethylene oxide.

Acetals are readily formed by the acid catalyzed reaction between ethyl alcohol and aldehydes and ketones.



Reaction with acrolein gives 3-ethoxypropionaldehyde as the initial product.



This is an example of 1,4-addition across a conjugated double bond system ($\text{C}=\text{C}-\text{C}=\text{O}$). Further reaction produces the acetal of the substituted propionaldehyde.

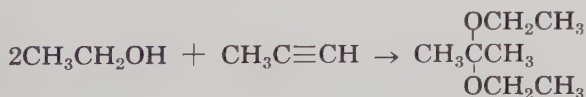
Vinyl ethyl ether is produced by the addition of ethyl alcohol to acetylene (402-408).



Potassium hydroxide and potassium ethoxide are catalysts for this reaction. The pressure is usually 200 to 300 psi and the temperature is between 160-180°C. The addition of alcohols to acetylene in the gas phase over contact catalysts has also been patented (409).

An extensive review of the preparation and properties of vinyl alkyl ethers has been published by Schildknecht, Zoss and McKinley (402). Vinyl ethyl ether can be polymerized readily by catalysts such as boron trifluoride, stannic chloride and aluminum chloride but it is polymerized slowly by free-radical initiators. It shows the general chemical behavior of an olefin.

The addition of ethyl alcohol to methylacetylene gives the diethyl acetal of acetone (a ketal) (410).



Amines can be produced from ethyl alcohol by its reaction with ammonia, and with primary or secondary amines. The various catalysts suggested include alumina alone or mixed with other metallic catalysts (411), phosphoric acid or a phosphate dispersed on a carrier (412) and oxides, chlorides, or sulfates of copper and iron in the presence of acids or alkaline salts (412). The vapor phase

reaction requires a temperature between 300° and 400°C. A reduced nickel catalyst at 200°C and 100 atms has been used for the reaction between ethyl alcohol and piperidine to give N-ethylpiperidine (413).

Acetone is normally produced directly from isopropyl alcohol or as a by-product in the production of both phenol and glycerol. Appreciable study, however, has been made on the formation of acetone by passing alcohol vapor and steam over a catalyst at a high temperature (414-416).

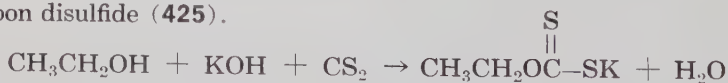


The various catalysts investigated include higher oxides of manganese (417), oxygen-containing compounds of iron, manganese, copper and calcium or magnesium (418), and calcium oxide-zinc oxide "cement" (419). Bakowski and Stepniewski report an 87% yield of acetone using 16.3 wt % alcohol over iron oxide plus calcium carbonate at 500°C (420).

The conversion of ethyl alcohol to ketones over a precipitated copper catalyst activated by thorium oxide gave only acetone at 280-320°C and a mixture of acetone (15%) and methyl propyl ketone (20%) at 330-380°C (421). Higher temperatures and increased reaction time gave predominantly condensation reactions with the production of dipropyl ketone, methyl amyl ketone and higher ketones to the extent of 8-10%. Bolotov, Dolgov and Katkova have proposed a mechanism for the formation of acetone and methyl propyl ketone under these conditions (422).

Ethyl mercaptan may be produced by an aluminum oxide catalyzed vapor-phase reaction between ethyl alcohol and hydrogen sulfide (423, 424).

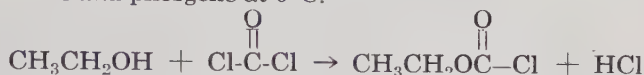
Ethyl xanthate is produced commercially by several processes. A German plant was reported after World War II to have made ethyl xanthate by the reaction of ethyl alcohol, potassium hydroxide and carbon disulfide (425).



A 400% excess of alcohol was used with 50% aqueous potassium hydroxide at 40°C. The yield was quantitative. The process can be modified to operate under anhydrous conditions (426, 427) or with

an inert diluent (428, 429). Xanthates are used by the mining industry as collector reagents in the flotation of various minerals.

Ethyl Chloroformate is readily produced by the reaction between ethyl alcohol and phosgene at 0°C.



When the conditions are strictly anhydrous a 90% yield is obtained. Ethyl chloroformate is a useful reagent for the introduction of the

carboxyethyl group ($\text{CH}_3\text{CH}_2\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$) into compounds with an active hydrogen. It can be used for the production of carbonates, polycarbonates, percarbonates and carbamates (urethanes), and other compounds which are used in pharmaceuticals, perfumes, flotation agents, plasticizers and resins.

Mercury fulminate [$\text{Hg}(\text{ONC})_2$] is produced by the reaction between mercury, ethyl alcohol and nitric acid. Mercury is dissolved in an excess of nitric acid and ethyl alcohol is added to the resulting mixture of mercuric nitrate and nitric acid. It is used as a detonator.

The *Guerbet reaction* consists in heating an alcoholic solution of a sodium alkoxide under pressure to effect condensation of the alcohol to higher molecular weight alcohols (430-435). A mixture of potassium hydroxide and boric anhydride has also been used as a catalyst (436, 437). Milder basic conditions have been patented which utilize potassium carbonate and copper chromite (438) and an alkaline phosphate (439) as catalysts.

Dvornikoff and Farrar have studied the condensation of ethyl alcohol to higher alcohols using a catalyst system employing magnesium oxide, potassium carbonate and copper chromite (440). A 20% conversion was obtained at 230°C after 8 hours. The major product was *n*-butyl alcohol. Small amounts of *n*-hexyl alcohol and 2-ethyl-1-butanol were also formed.

n-Butyl alcohol has also been obtained by passing ethyl alcohol vapors at about 325°C over a catalyst composed of 40% CuO and 60% MgO or 20% CuO and 80% MgO (441). Other catalysts patented for this same general process are magnesia with a smaller proportion of copper (442), magnesia and chromic oxide (443), iron oxides and aluminum precipitated on powdered animal charcoal (444). Higher molecular weight alcohols are formed along with the *n*-butyl alcohol. A mixture of ethyl alcohol and *n*-butyl alcohol over a mixed catalyst

of aluminum, uranium and thorium oxides with copper, silver, nickel or chromium gave hexyl alcohol as the main product (445).

Alkylation of various compounds by ethyl alcohol using sodium ethoxide as the catalyst was noted in the discussion of sodium ethoxide. The general area of base-catalyzed alkylations with alcohols has been the subject of a review article by Becker (1959) (446).

The *action of heat and pressure* on ethyl alcohol leads to a variety of products depending upon the temperature and pressure (447). Smolenski reports that gases are the main product at 350°C but 80% of the products are liquid at 400°C (448, 449). The liquid products are chiefly oxygenated. At 450°C there is a 40% yield of liquids and they contain a large proportion of cyclic hydrocarbons. The various products of *Catalytic decomposition* of ethyl alcohol have been investigated extensively by Boomer and Morris (450). They were especially interested in the formation of methane, ethane and carbon dioxide. The results of these studies have been summarized by Ellis (96). The action of Raney nickel on ethyl alcohol at 225-280°C and 100-240 kg/cm² pressure gave 10-15% carbon dioxide, 1% oxygen, 4% carbon monoxide, 1-2% hydrogen, 80% methane and some acetaldehyde, diethyl acetal and *n*-butyl alcohol (451). The action of Raney copper on ethyl alcohol at high temperature and pressure gives an azeotrope of ethyl acetate and ethyl alcohol as the chief product along with a very small amount of acetic acid (452).

OTHER REACTIONS AND DERIVATIVES

The following miscellaneous reactions were picked at random from the literature to indicate the versatility of ethyl alcohol. It would be virtually impossible to list all the reactions of ethyl alcohol and all of its derivatives.

Carbon dioxide from ethyl alcohol over an oxide catalyst (453).

Rates of alcoholysis and diffusion in ion-exchange resins (454).

Study of adsorption and surface reactions of ethyl alcohol on aluminum oxide by the method of infrared spectroscopy (455).

Inclusion compounds with halloysite and montmorillonite (456).

Synthesis of ethanol-1-C¹⁴ and ethanol-2-C¹⁴ (457).

Formation of beta-chloroethyl ether (458).

Reaction with boron trifluoride (459).

Preparation of sodium acetate (460).

Catalytic hydrogenation of toluene by means of ethyl alcohol (461).

Effect of electric arc or spark on ethyl alcohol vapor (462).

Reaction with *p*-nitrobenzoyl chloride in nitrobenzene at 7.38°; kinetic study (463).

Opening of the epoxide ring of 1,1,1-trifluoro-2,3-epoxypropane (464).

Etherification of monomethylolurea (465).

Reactions of phenyl isocyanate and ethyl alcohol (466).

Reaction of perhalomethanes and ethyl alcohol (467).

Reduction of tolan by metals in ethyl alcohol (468).

Behavior of 3-nitro-4-thiocyanopyridine with ethyl alcohol (469).

Reaction with ammonium chloride to form ethyl chloride (470).

Continuous chlorination of ethyl alcohol (471).

Adsorption on activated carbon and silica gel (472).

Catalytic decomposition of $\text{CH}_3\text{CD}_2\text{OH}$ (473).

Reaction of acetyl benzoyl peroxide with ethyl alcohol (and others) (474).

Reaction with quinquivalent compounds of uranium (475).

Adsorption of ethyl alcohol (and others) on mercury (476).

Kinetics of the alcoholysis of *o*- and *p*-nitroacetanilides (477).

Alcoholysis of silylphosphine (478).

Adsorption and surface reactions of ethyl alcohol on aluminum oxide (479).

Addition of ethyl alcohol (and others) to α -ethylenic α -alkoxy-nitriles (480).

Decomposition of ethyl alcohol (and others) over a Fischer-Tropsch iron catalyst (481).

Sulfur dioxide-ethyl alcohol complexes (482).

Ethyl alcohol induced photolysis of hydrogen peroxide (483).

Chemisorption of ethyl alcohol (and others) on amorphous silica (484).

Iodine complexes with ethyl alcohol (and others) in carbon tetrachloride (485).

Reaction of ethyl alcohol with benzenesulfonyl fluoride to produce ethyl fluoride (486).

Mechanism of alkylation of ethyl alcohol (and others) by *N,N,N*-trimethyl-1-phenethylammonium iodide (487).

Reaction of stannic chloride with ethyl alcohol (and others) (488).

Acetaldehyde by refluxing absolute alcohol with U.O.P. nickel catalyst (489).

Ascorbic and dehydroascorbic acids in the presence of ferric ion catalyzes the oxidation of ethyl alcohol by hydrogen peroxide (490).

Acetaldehyde in a 50% yield by oxidation of ethyl alcohol by solid manganese dioxide (491).

Oxidation of ethyl alcohol by ceric perchlorate (492).

APPLICATIONS AS A SOLVENT

Ethyl alcohol is the most important organic solvent and is second only to water in its diversity of applications (Table XVI). It is used as a solvent in surface coatings, cosmetics, aerosols, pharmaceuticals, flavoring preparations, plastics and explosives. Large amounts are used in cleaning preparations and in the dehydration of nitrocellulose. It is also used as an extraction agent, as a solvent for purification by crystallization, and it may serve as a carrier or vehicle for a variety of materials. The list of solvent applications could be expanded almost indefinitely.

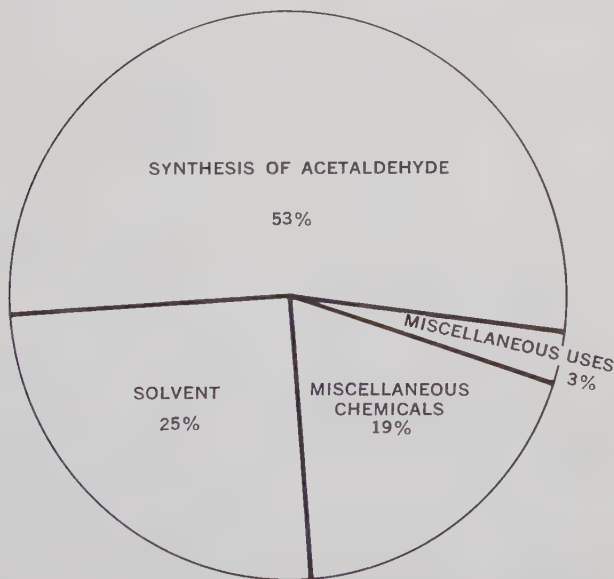


Figure 8. General end-use pattern for ethyl alcohol (1960).

Table XVI
USES OF SPECIALLY DENATURED ALCOHOL
AS A SOLVENT DURING FISCAL YEAR ENDED
JUNE 30, 1960
(325)

Product or Use	Quantities in Wine Gallons		
	New Alcohol Used ¹	Recovered Alcohol Used ²	Alcohol Recovered For Use
USED AS A SOLVENT:			
Cellulose, resin, and related products:			
Lacquers, varnishes, and enamels:			
Cellulose	190,136	503,402	503,125
Synthetic resin (with or without natural resins but containing no cellulose compounds)	852,314	3,406	—
Shellac (containing no cellulose or synthetic resins)	2,393,771	—	—
Other natural resins (containing no cellulose, synthetic resin, or shellac)	78,209	—	—
Candy glazes	155,109	—	—
Other coatings	<u>41,200</u>	<u>131,197</u>	<u>122,529</u>
Total	3,710,739	638,005	625,654
Plastics:			
Cellulose compounds	1,335	70,050	71,600
All other plastics (containing no cellulose)	<u>2,223,184</u>	—	—
Total	2,224,519	70,050	71,600
Photographic film (including emulsions)	304,072	94,769	104,943
Transparent sheeting	212,029	1,297,723	1,426,395
Cellulose intermediates	16,812	—	—
Explosives	654,114	4,707,981	4,723,748
Polishes	7,072	—	—
Adhesives	332,228	5	—
Soldering flux	18,227	—	—
Inks, stains, and dye solutions (containing no cellulose or resins)	<u>73,897</u>	—	—
Total cellulose, resin, and related products	7,553,709	6,808,533	6,952,340

Table XVI (continued)
USES OF SPECIALLY DENATURED ALCOHOL
AS A SOLVENT DURING FISCAL YEAR ENDED
JUNE 30, 1960

Product or Use	Quantities in Wine Gallons		
	New Alcohol Used ¹	Recovered Alcohol Used ²	Alcohol Recovered For Use
Solvents and thinners for cellulose, shellac, resin products, etc.:			
Proprietary solvents	21,473,127	14,620	12,350
Other industrial thinners	<u>3,075,441</u>	<u>76</u>	<u>—</u>
Total	24,548,568	14,696	12,350
Toilet preparations:			
Hair and scalp preparations	4,045,266	12,528	12,629
Bay rum	73,477	—	—
Face and hand lotions	2,813,667	—	—
Body deodorants	908,292	—	—
Perfume and perfume tinctures	120,025	—	—
Toilet waters	2,692,697	—	—
Tooth cleaning preparations	2,738	—	—
Mouth washes and oral antiseptics ..	704,854	—	—
Shampoos	220,757	—	—
Toilet soaps (including shaving creams)	<u>39,157</u>	<u>—</u>	<u>—</u>
Total	11,620,930	12,528	12,629
Processing industrial, food, drug, and other products:			
Nitrocellulose (dehydration)	4,067,949	14,650,043	14,642,031
Sodium hydrosulphite	813,201	15,292,634	16,705,260
Petroleum oils	786,178	7,236,366	7,247,235
Food products other than pectin	41,191	421,509	423,973
Drug products:			
Drug extracts	63,649	457,157	398,767
Glandular products, vitamins, antibiotics, and blood products	1,249,439	8,235,451	7,378,781
Medicinal chemicals	970,017	1,199,544	1,417,669
Miscellaneous (including pill and tablet manufacture)	269,136	32,984	55,571

Table XVI (continued)
USES OF SPECIALLY DENATURED ALCOHOL
AS A SOLVENT DURING FISCAL YEAR ENDED
JUNE 30, 1960

Product or Use	Quantities in Wine Gallons		
	New Alcohol Used ¹	Recovered Alcohol Used ²	Alcohol Recovered For Use
USED AS A SOLVENT (Continued)			
Dyes and intermediates	480,972	358,022	434,388
Perfume materials and fixatives	17,316	16,952	16,509
Photographic developers	169,638	53,694	61,916
Rosin processing	234,020	7,898,983	7,849,385
Rubber processing	42,904	—	—
Miscellaneous chemicals	384,358	1,349,511	1,316,511
Miscellaneous	293,695	22,282	126,321
Total	9,883,663	57,225,132	58,074,317
Pharmaceutical products for external use:			
Rubbing alcohol	2,010,587	2,700	270
U.S.P. and N.F. preparations:			
Witch hazel	120,529	—	—
Liniments	69,558	—	—
Collodions	6,641	—	—
Antiseptics	9,612	—	—
Miscellaneous	15,593	—	—
Total	2,232,520	2,700	270
Tinctures of iodine (official and non-official)	34,482	—	—
Other preparations not U.S.P. or N.F. . .	1,837,236	—	—
Total pharmaceutical products for external use	1,871,718	—	—
Cleaning, preserving, and flavoring preparations:			
Tobacco sprays and flavors	1,141,974	—	—
Cleaning preparations (including home detergents) and cleaning operations .	8,139,904	14,221	10,290

Table XVI (continued)
USES OF SPECIALLY DENATURED ALCOHOL
AS A SOLVENT DURING FISCAL YEAR ENDED
JUNE 30, 1960

Product or Use	Quantities in Wine Gallons		
	New Alcohol Used ¹	Recovered Alcohol Used ²	Alcohol Recovered For Use
Deodorant sprays (non-body)	287,107	—	—
Disinfectants, insecticides, etc.	182,487	—	—
Sterilizing and preserving solutions . .	29,681	—	—
Embalming fluids & related products	17,055	—	—
Industrial soaps	31,954	—	—
Photoengraving and rotogravure use .	55,639	—	—
Miscellaneous	714,892	—	2,913
Total	10,600,693	14,221	13,203

¹ Represents quantity of alcohol used for the first time, whether or not any quantity is subsequently recovered.

² Represents quantity of alcohol reused after recovery from processes where the alcohol has not become a part of the finished products. Such alcohol may have been recovered during the fiscal year 1960 or prior thereto and from any of the listed processes.

Surface Coatings

NITROCELLULOSE LACQUERS

Although it is not in itself a true solvent for nitrocellulose, ethyl alcohol increases the solvent power of active ketone and ester solvents for this material. In its role as a *latent solvent*, it helps to produce solutions of lower viscosity for a given nitrocellulose concentration, as shown in Figure 9 (493). Ethyl alcohol's incorporation into a solvent blend also increases the amount of low-cost hydrocarbon diluent the solvent blend will tolerate before the nitrocellulose is precipitated. The ability of an active solvent to tolerate such diluents is expressed as *dilution ratio*—the volumes of diluent per unit volume of active solvent which just fails to precipitate nitrocellulose, generally determined at a concentration of 8 grams of nitrocellulose per 100 ml of the combined solvents (493-497).

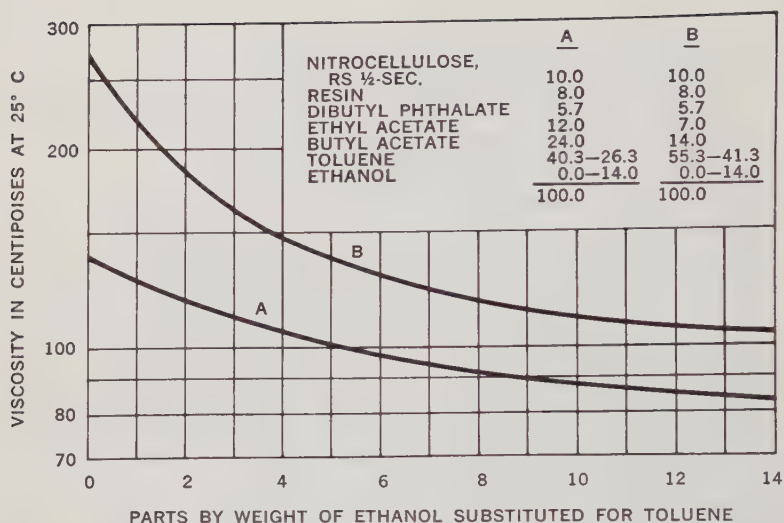


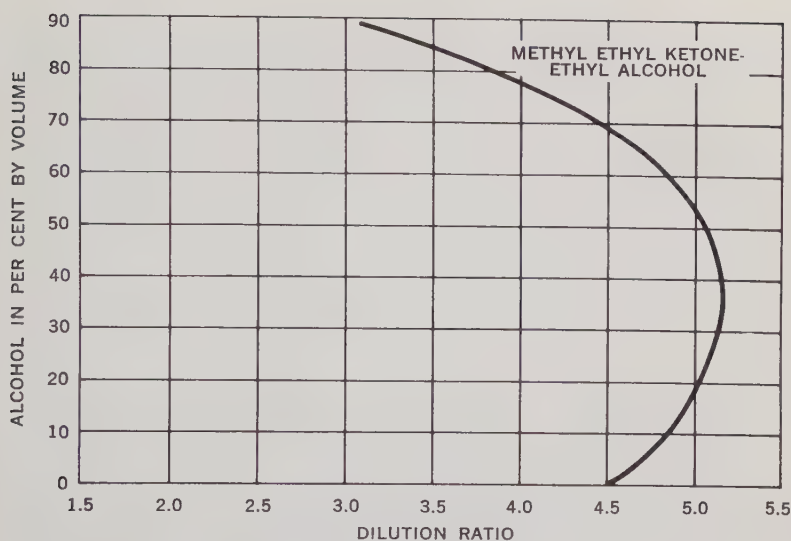
Figure 9. Effect of ethyl alcohol on the viscosity of nitrocellulose solutions. (From "Nitrocellulose Properties and Uses," Hercules Powder Company, Wilmington, Delaware, 1955; page 17.)

Figure 10 demonstrates the effect of ethyl alcohol on the toluene dilution ratio of methyl ethyl ketone. Diluents should not be confused with *thinners*, which are balanced solvent blends that can be added to a base lacquer solution in any quantity without impairing the solvency of the system.

Most nitrocellulose lacquers are applied at about 27% solids by standard spray techniques at room temperature. Cold-spray solvent blends are usually made up as follows (493):

	Per Cent
<i>Active Solvent</i> (i.e. ethyl acetate, butyl acetate, methyl ethyl ketone)	20-50
<i>Alcohol Cosolvent</i> (i.e. ethanol, isopropanol, butanol)	10-25
<i>Diluent</i> (i.e. toluene, xylene, aliphatic hydrocarbon)	30-60

Similar blends are used in formulating hot-spray lacquers, except that higher-boiling solvents are used (495, 498). Hot-spray lacquers have higher solids content (up to 40%) than cold-spray lacquers, as well as other advantages. A typical hot-spray solvent blend is as follows (499):



Nitrocellulose Concentration:
2 grams dry $\frac{1}{2}$ sec. RS N/C per 20 cc solvent.

Figure 10. Effect of ethyl alcohol on the toluene dilution ratio of methyl ethyl ketone.

	<i>Per Cent</i>
Methyl isobutyl ketone	37.5
Ethyl alcohol (S.D.A. 2B)	10.0
<i>n</i> -Butanol	12.5
Xylene	40.0

Brushing lacquers are used for general refinishing of wood or metal surfaces. Good brushability and other desirable properties in a clear, plasticized nitrocellulose lacquer may be obtained at 30% solids using the following solvent blend as a starting formula (500):

	<i>Parts by Weight</i>
Ethylene glycol monoethyl ether acetate	35
Ethyl alcohol	10
Isopropyl alcohol	10
Turpentine	45

In addition to its use in lacquers for rigid surfaces, ethyl alcohol also finds use in nitrocellulose solutions for coating textiles to produce artificial leather, waterproof book-cover cloth and other products.

Dope solutions containing 15-20 second nitrocellulose have been studied in detail by Doolittle (495). Unlike metal and wood lacquers, textile coating compositions usually do not contain modifying resins. A high proportion of plasticizer is used, however, as shown in the following typical formula (493).

	<i>Parts by Weight</i>
RS Nitrocellulose, 30-40 sec. (dry wt) ..	14.0
Plasticizer	21.0
Carbon black	0.7
Ethanol	12.9
Toluene	25.7
Ethyl acetate	19.3
Butyl acetate	6.4
Total	100.0

The fact that commercial nitrocellulose is usually sold wet down with 30% by weight of ethyl alcohol must be taken into account when blending coating solutions.

MIXED CELLULOSE ESTERS

Ethyl alcohol is used in solvent blends for lacquers based on cellulose acetate-propionate and cellulose acetate-butyrate (501, 502). A typical thinner blend for these mixed esters is as follows:

	<i>Per Cent</i>
Ethyl acetate	10
<i>n</i> -Butyl acetate	20
Ethyl alcohol	20
<i>n</i> -Butyl alcohol	10
Toluene	40

ETHYLCELLULOSE

Ethylcellulose is one of the most versatile film-forming cellulose-based resins. The blending of solvents for this resin has been investigated by Philippoff (503) and by Kauppi and Bass (504, 505). The mechanical properties of ethylcellulose films are greatly influenced by the composition of the solvent mixture from which they are deposited; the most practical solvent combination is a mixture of toluene and ethyl alcohol. The proportion of ethyl alcohol is quite critical, since an alcohol content too high will cause loss of film strength while a content too low will give solutions of excessively

high viscosity. Maximum film strength and minimum viscosity occur at an alcohol concentration of 30% by volume (504). Twenty per cent ethyl alcohol is usually recommended, however, because the finishes produced from this solvent mixture are more blush-resistant.

A small amount of water slightly increases the solvent ability of the ethyl alcohol; thus, 95% alcohol is used in preference to absolute alcohol. It is desirable to include some xylene and butyl alcohol in the solvent for spray applications. The proportion of hydrocarbon to alcohol is maintained at about 80:20. The same solvent proportion is used for coating solutions based on *benzylcellulose*.

ACRYLICS

Ethyl alcohol reduces the solution viscosity and helps prevent cobwebbing of spray-applied acrylic coatings. The alcohol itself is not actually a solvent for acrylics but it improves the performance of the hydrocarbon solvents it is blended with. The following formula is for a pigmented metal lacquer suitable for airless hot-spray application (506):

<i>Solids Composition</i>	<i>Weight Per Cent</i>
Acryloid B-82 ¹	35.7
RS Nitrocellulose, ½ sec. ²	16.3
Santicizer 160 ³	13.0
Rutile titanium dioxide	35.0
Total	100.0

<i>Solvent Composition</i>	
Methyl isobutyl ketone	20.0
Methyl ethyl ketone	20.0
Ethylene glycol monoethyl ether acetate	10.0
Butanol	5.0
Ethanol	5.0
Xylene	20.0
Toluene	20.0
Total	100.0

¹ Rohm & Haas Company

² Hercules Powder Company

³ Monsanto Chemical Company

VINYL RESINS

Ethyl alcohol is generally not suitable as a solvent for polyvinyl chloride or vinyl chloride-vinyl acetate copolymer. The partially hydrolyzed copolymer is an exception, however, and small amounts of ethyl alcohol are used in solvent blends for this material.

Ethyl alcohol has also been recommended for use in wash primers or metal conditioners containing phosphoric acid, zinc chromate and polyvinyl butyral resin (507). Polyvinyl acetates are relatively soluble in alcohols.

SILICONES

Silicone resins are relatively low molecular weight in the form in which they are applied to a surface before heat treatment. These resins are soluble in nearly all solvents except markedly hydrophilic types. The preferred solvents are toluene, xylene or cycloparaffins, mixed with a small amount of ethyl alcohol (495).

SHELLAC AND OTHER SPIRIT VARNISHES

Ethyl alcohol is the most satisfactory and widely used solvent for shellac. During fiscal year 1960, 2.4 million gallons of specially denatured alcohol were used for this purpose. In addition, a significant part of the 21.4 million gallons of proprietary alcohol solvents manufactured that year also was used in shellac solutions.

Shellac dissolved in alcohol produces a solution which dries quickly to form a smooth, glossy, wear-resistant coating with good adhesion to most surfaces. Besides protective coatings, some other uses for shellac are in floor finishes, adhesives, electronic parts, pills and candy glazes.

Considerable swelling and bulking occurs when shellac is added to ethyl alcohol. For example, a 4-pound cut of shellac contains 4 pounds of dry shellac dissolved in one gallon of alcohol. But the resultant volume of this mixture is 1.4 gallons, with a shellac solids content of 2.86 pounds per gallon of solution.

Other oxygenated solvents are sometimes combined with alcohol in solvent blends for shellac. Mixed solvents for shellac have been investigated by Palit (508).

Ethyl alcohol is also used as a solvent in spirit varnishes based on other natural resins. Kauri gum, manilas, dewaxed damar, elemi, sandarac and other resins will dissolve in alcohol to form solutions with practical solids contents and working viscosities. The book

“Technology of the Natural Resins” (1942) contains material related to the solvent characteristics of ethyl alcohol for natural resins (509).

MISCELLANEOUS COATING APPLICATIONS

Ethyl alcohol is used in many types of surface coatings not specifically mentioned above. It is part of the solvent formulation for epoxy-phenolic chemical-resistant coatings. It is also used in epoxy-urea based bronze or aluminum powder coatings, as well as in other synthetic resin-blend systems. Greaseproof and decorative paper coatings based on zein employ ethyl alcohol (507). Resin penetration into absorbent papers has been studied by Arledter in respect to a number of variables, including the use of ethyl alcohol as a solvent (510). Although it is not a solvent for crude rubber, small amounts of ethyl alcohol have the effect of reducing the viscosity of its hydrocarbon solutions (511). Such solutions are used for coating fabrics to make conveyor belts, rainwear and other products.

Cosmetics and Toiletries

Today, as in centuries past, ethyl alcohol is widely used in all manner of cosmetic and toilet preparations. Over 11.6 million gallons of specially denatured alcohol were used for this purpose during fiscal year 1960. Primary among ethyl alcohol’s many qualifications for these products is its excellent solvency for essential oils, perfumes and other substances (Table XVII). Another important property is its compatibility with other solvents commonly used in cosmetics and toiletries. Also important are ethyl alcohol’s antiseptic and astringent properties, as well as its relatively mild odor and taste.

TOILET WATERS AND PERFUMES

About 2.8 million gallons of specially denatured alcohol were used in toilet waters and perfumes during fiscal year 1960. The most popular of the toilet waters are Eau de Colognes, which in general are citrus bouquets blended with other perfumes. The following is given by Poucher as having the traditional Eau de Cologne fragrance (512):

<i>Place in a still</i>	
Bergamot oil	8
Lemon oil	6
Sweet orange oil	5

Lavender oil, French	1
Orris root, crushed	10
Alcohol, 90%	500
Water	70
	<hr/>
	600

Macerate for 24 hours and then distil slowly. Collect 500 cc in the receiver and to this add:

Neroli oil, bigarade	2.5
Rosemary oil	0.5
Benzoin R.	5
Alcohol, 90%	500
	<hr/>
	508

Mature one month.

Poucher also lists the following cheap cologne (512):

Linalyl acetate	600
Citral	200
Aurantiol	50
Ceylon citronella	30
Terpinyl acetate	50
Rosemary, Spanish	50
Musk xylene	20
	<hr/>
	1000

Use 1 or 2% in weak alcohol.

Other types of toilet waters also make abundant use of ethyl alcohol. The following formula is for a good quality Lavender Water (512):

Lavender oil, English	20
Bergamot oil	10
Tincture of musk	5
Tincture of orris	5
Alcohol, 90%	1000
	<hr/>
	1040

Mature for at least six months and filter if necessary.

SKIN LOTIONS

Ethyl alcohol is used in many types of lotions for the face, hands and body. A large market exists for after-shave lotions such as the following listed by Keithler (513):

	<i>Per Cent</i>
Alcohol	40.0
Menthol	0.2
Sorbitol	2.0
Boric acid	2.0
Benzoic acid	1.0
Fougere	0.3
Water	54.5

Pre-electric shave lotions containing hexachlorophene, isopropyl myristate, glycerin, perfumes and other materials also use high percentages of ethyl alcohol. It is also used in bay rum and various other lotions to freshen and invigorate the skin.

Hand lotions based on glycerin sometimes employ ethyl alcohol as a solvent for the perfume constituent of the formulation. Alcohol is also used in liquid make-up for the face and legs, as well as in sun-tan and sun-screen lotions. Liquid toilet soaps and shaving creams sometimes contain ethyl alcohol. It is often an ingredient of aerosol-dispensed lotions.

HAIR AND SCALP PREPARATIONS

Ethyl alcohol has been a vehicle for the dyes, oils, soaps and gums used in treating the hair for many centuries. It still plays a leading role in this art; over 4 million gallons of specially denatured alcohol were used in hair and scalp preparations during fiscal year 1960. The following selection is representative of the innumerable alcohol-containing formulations for hair dyes, tonics, shampoos, lotions, and wave-setting compositions (lacquers) in current use.

Hair Dye	<i>Per Cent</i>
Irgalan Brown 2GL 230% ¹	0.3
Methocel HG-60 ² (for viscosity if desired) ...	1.0
Ethyl alcohol	15.0
Water	82.7
Acetic acid	1.0

¹ Geigy Chemical Corporation

² Dow Chemical Company

Hair Tonic (513)	<i>Per Cent</i>
Alcohol	88.50
G-4 ¹	0.25
Oxyquinoline benzoate	1.00
Oil of eucalyptus	2.00
Salicylic acid	0.25
Olive oil	8.00

¹ Sindar Corporation

Coconut Oil Shampoo (513)	<i>Per Cent</i>
Olive Oil	3.0
Coconut oil	21.0
Caustic potash, 85%	4.1
Caustic soda, 95%	1.9
Alcohol	15.0
Distilled water	54.0
Perfume	0.5
Ethylenediamine Tetra-acetic Disod.	0.5

Aerosol Hair-Setting Spray (514)	<i>Parts by Weight</i>
Polyvinylpyrrolidone (PVP K30 ¹)	2.0
Alcohol-soluble lanolin	0.5
Perfume oil	0.3
Ethanol, S.D.A. 40 anhydrous	22.2
Propellents 11/12 (70/30)	75.0

¹ Antara Chemicals Div. General Aniline & Film Corp.

To improve flexibility and reduce hygroscopicity of the resultant PVP film, a compatible plasticizer such as dimethyl phthalate, glyceryl monoricinoleate, or oleyl alcohol may be added (10-25% based on resin solids).
See also (515) and (516).

Quite in contrast to its role in hair-beautifying preparations, ethyl alcohol is also used in depilatory compositions to remove unwanted hair.

MOUTH WASHES

Many mouth washes and oral antiseptics contain ethyl alcohol in percentages ranging from 10 to 50%. The following formulation is typical (513):

	<i>Per Cent</i>
Alcohol, S.D.A. 38-B	23.4
Benzoic acid	1.1
Boric acid	3.0
Menthol	0.1
Eucalyptus	0.3
Eucalyptol	0.3
Thymol	0.1
Water	71.6
Caramel color	0.1

Some ethyl alcohol is also used in liquid dentrificates.

DEODORANTS AND ANTI-PERSPIRANTS

Ethyl alcohol is an ingredient of deodorants and anti-perspirants formulated for application in spray, lotion, cream and stick forms. Keithler gives the following formulation for a deodorant stick (513):

Alcohol, S.D.A. 39-C	56.00 ml
Distilled water	4.00 ml
Propylene glycol	5.00 gm
Sodium stearate	4.25 gm
Perfume	0.20 gm
Hexachlorophene	0.14 gm

An anti-perspirant composition suitable for spray application is described in a 1959 patent (517):

	<i>Per Cent</i>
Sodium zirconium lactate (43% soln.)	20
Zirconium lactate	2
Polyethylene fatty alcohol	0.3
Propylene glycol	10
Alcohol, S.D.A. 40	20
Water	47.7
Perfume	Q.s.

Flavoring Preparations

Ethyl alcohol is used in the processing of many common flavoring materials. In addition, it is often an ingredient of the extracts and essences prepared from these materials for use in foods. Manufac-

turers of flavoring preparations which are unfit for beverage purposes may obtain a refund of Federal taxes paid on any pure ethyl alcohol they use in their products.

Vanilla is one of the most universally used flavoring materials. This product is an ethyl alcohol solution of the plant's aromatic principle, vanillin, obtained from the ground vanilla bean. Synthetic vanillin has now replaced the natural product to a large extent, but ethyl alcohol still has a role in its manufacture. A typical commercial vanilla extract contains about 35% alcohol.

Some other flavoring substances which employ ethyl alcohol in their manufacture are cinnamon, cloves, ginger, licorice and peppermint. Table XVII lists the solubility in 90% and 45% ethyl alcohol of various essential oils, used either as flavorings or as cosmetics ingredients.

Table XVII
SOLUBILITY IN ETHYL ALCOHOL OF ESSENTIAL OILS
AND SYNTHETIC MATERIALS USED IN
FLAVORS AND PERFUMES
(518)

Volumes of ethyl alcohol required to dissolve one volume of oil

All = less than 1/10 volume alcohol per volume oil

Blank = more than 1,000 volumes alcohol per volume oil

Essential Oils	Ethyl Alcohol 90%	Ethyl Alcohol 45%
Almond	All	22.0
Ambrette seed	1.0	—
Anise	3.0	250.0
Bay	1.0	200.0
Bergamot	1.0	400.0
Bergamot, terpeneless	All	180.0
Cajuput	5.0	190.0
Cananga	1.5	500.0
Caraway	1.0	195.0
Cardamoms	1.0	80.0
Cassia	1.0	150.0
Cedarwood	12.0	500.0
Celery	10.0	—
Cinnamon bark	0.3	92.0

Table XVII (continued)
SOLUBILITY IN ETHYL ALCOHOL OF ESSENTIAL OILS
AND SYNTHETIC MATERIALS USED IN
FLAVORS AND PERFUMES

Essential Oils	Ethyl Alcohol 90%	Ethyl Alcohol 45%
Cinnamon leaf	All	100.0
Citronella, Java	1.0	165.0
Clove	All	80.0
Cognac	All	225.0
Coriander	0.5	200.0
Dill	3.0	100.0
Eucalyptus	5.0	210.0
Fennel	1.0	200.0
Geranium, African	All	200.0
Gingergrass	1.0	125.0
Juniper	4.0	210.0
Lavender, French	2.5	100.0
Lavender, terpeneless	All	90.0
Lavender, spike, Fr.	2.0	150.0
Lemon	4.0	200.0
Lemon, terpeneless	All	170.0
Lemongrass	14.0	85.0
Limes, Dist.	4.5	75.0
Linaloe	2.0	100.0
Neroli, Bigarad	2.0	100.0
Nutmeg	3.0	130.0
Orange, bitter	10.0	150.0
Orange, bitter, terpeneless	6.0	210.0
Orange, sweet	10.0	210.0
Orange, sweet, terpeneless	6.0	250.0
Orris, concrete	1.0	—
Otto Rose (filtered)	All	250.0
Palmarosa	3.0	100.0
Patchouli	10.0	500.0
Pepper	7.0	—
Peppermint, Amer.	All	150.0
Peppermint, Jap.	2.0	180.0
Petitgrain	2.0	100.0
Petitgrain, terpeneless	All	150.0
Pimento	All	50.0
Pine, sylvest	3.0	—
Rose, Femelle	1.0	100.0
Rosemary, Fr.	2.0	100.0
Rosemary, Fr., terpeneless	All	100.0
Rue	All	120.0
Sage	2.0	100.0
Sage, Sclarae	2.0	—
Sandal, E. I.	5.0	160.0
Sassafras	3.0	200.0
Spearmint	1.0	—

Table XVII (continued)
SOLUBILITY IN ETHYL ALCOHOL OF ESSENTIAL OILS
AND SYNTHETIC MATERIALS USED IN
FLAVORS AND PERFUMES

Essential Oils	Ethyl Alcohol 90%	Ethyl Alcohol 45%
Thyme, rouge	1.0	200.0
Vetivert	2.0	—
Ylang	0.75	100.0
Synthetic Materials	Ethyl Alcohol 90%	Ethyl Alcohol 45%
Acetic ether	All	All
Acetophenone	All	8.0
Amyl Acetate	All	21.0
Amyl valerate	All	180.0
Anethol	2.0	100.0
Anisic Aldehyde	All	30.0
Benzaldehyde	1.0	15.0
Benzyl acetate	1.0	35.0
Benzyl alcohol	1.0	2.0
Benzyl benzoate	2.0	—
Benzyl butyrate	All	70.0
Benzyl formate	All	29.0
Benzyl valerate	All	130.0
Benzylidene acetone	0.25	8.0
Bornyl acetate	All	200.0
Bromstyrol	5.0	500.0
Butyl acetate	All	9.0
Cinnamic alcohol	All	7.5
Citral	1.0	—
Citronella	1.0	—
Citronellol	1.0	40.0
Citronellyl acetate	All	330.0
Coumarin	6.0	35.0
Ethyl-cinnamate	All	140.0
Eugenol	All	8.0
Geraniol	1.0	50.0
Geranyl acetate	All	800.0
Geranyl butyrate	All	560.0
Heliotropin	2.5	33.0
Ionone	All	110.0
Ionone alpha	All	60.0
Iso-eugenol	All	30.0
Jasmin art.	All	70.0
Linalol	1.0	18.0
Linalyl acetate	1.0	200.0
Linalyl butyrate	All	180.0

Table XVII (continued)
SOLUBILITY IN ETHYL ALCOHOL OF ESSENTIAL OILS
AND SYNTHETIC MATERIALS USED IN
FLAVORS AND PERFUMES

Synthetic Materials	Ethyl Alcohol 90%	Ethyl Alcohol 45%
Methyl acetophenone	1.0	14.0
Methyl anisate	2.0	32.0
Methyl anthranilate	5.0	20.0
Methyl benzoate	All	—
Methyl salicylate	1.0	166.0
Mirbane	All	75.0
Musk ambrette	100.0	—
Musk xylol	250.0	—
Neroli art.	2.0	300.0
Nerolin	50.0	666.0
Oenanthic ether	All	—
Phenyl acetic acid	0.75	1.4
Phenyl acetic aldehyde	All	—
Phenyl ethyl alcohol	All	4.5
Phenyl oxide	5.0	300.0
Phenyl propyl alcohol	All	260.0
Rhodinol	1.0	160.0
Safrol	10.0	300.0
Salicyl amyl	3.0	500.0
Styrolyl valerate	All	150.0
Terpineol	1.0	30.0
Terpinyl acetate	1.0	—
Terpinyl propionate	All	110.0
Vanillin	2.5	10.0

Tobacco Sprays and Flavors

An alcohol solution of various perfumes and flavors is used to impart desirable properties to cured tobacco before it is made into cigarettes, pipe tobacco and cigars. Over one million gallons of S.D.A. 4 were used for this purpose during fiscal year 1960. In addition to this specially denatured alcohol, an approximately equal amount of denatured rum was used for the same purpose during the same period.

In manufacturing cigarettes, the cured tobacco leaf is damped, its midrib is removed, and it is cut into thin strips. At this stage, the tobacco is sometimes heated to remove excess moisture and to help develop its natural aroma and taste. It is then sprayed with a mixture of various perfumes and flavors in ethyl alcohol. The alcohol

is allowed to evaporate and the flavored tobacco is processed into cigarettes. Some of the substances used in cigarette sprays are coumarin, cascarilla oil, geranium oil, valerian, orris, sweet orange oil, vanilla, rose otto, lavender oil, bergamot oil and clove oil.

In cigar manufacture, the stripped, cured leaf is generally sprayed with cascarilla-coumarin type scents. Rum or brandy is often used along with ethyl alcohol as the spraying vehicle. Cigar boxes are also sometimes sprayed to improve their fragrance. Cedarwood oil, sandalwood oil and other perfumes are used for this purpose.

Pharmaceuticals and General Medical Use

Ethyl alcohol is used in an enormous variety of pharmaceutical products for both external and internal use. The Pharmacopoeia of the United States, The National Formulary and other publications list hundreds of medical preparations which employ various strengths of both pure and denatured ethyl alcohol. Federal law permits a refund of taxes on pure ethyl alcohol used in medicinal products which are unfit for beverage purposes.

Hospitals and medical laboratories find many important daily uses for this vital liquid. Such organizations are permitted by law to obtain tax-free pure ethyl alcohol.

GERMICIDAL AND OTHER PROPERTIES

Many of the medicinal uses of ethyl alcohol depend on its germicidal powers. In proper concentrations, it will quickly kill most pathogenic bacteria. Some spore-bearing bacterial organisms, however, are resistant to alcohol. It is generally contended that about 70% by weight in water is its most effective concentration for local antisepsis (519, 520). Some studies have shown, however, that 95% ethyl alcohol is more effective in destroying bacteria on the skin (521, 522). There is an extensive medical literature on the germicidal properties of alcohols (523-535, and others).

Other properties of ethyl alcohol that make it useful in pharmaceuticals are its mildly irritant effect, its astringency, its drying ability and its cooling effect on evaporation. Of primary importance of course is its excellent solvency for countless drugs and other substances. Still other properties of ethyl alcohol which sometimes lead to its use in the practice of medicine are its very mild anesthetic

nature, its effect as a circulatory stimulant, its nutritive value, and its emotionally stimulating initial effects when imbibed. The toxicological properties of ethyl alcohol are discussed in Chapter Six.

PHARMACEUTICALS FOR EXTERNAL USE

Over 2 million gallons of specially denatured alcohol were used in rubbing alcohol compounds during fiscal year 1960. All rubbing alcohol compounds are manufactured with S.D.A. 23-H according to the following formula (309):

S.D.A. No. 23-H	103.3 fl. oz.
Sucrose octa-acetate	0.5 av. oz.
Water (and odorous or medicinal ingredients) q.s.	1 gal.

Manufacturers may add to the formula other odorous or medicinal ingredients if they are shown in the formula submitted to the Alcohol and Tobacco Tax Division of the Internal Revenue Service for approval. The finished product must contain 70% absolute alcohol by volume. If a preparation intended for use as a rubbing alcohol compound is produced from any other material, such as isopropyl alcohol, it must not be labeled "Rubbing Alcohol Compound" without the label clearly indicating that it was not made with specially denatured alcohol.

Ethyl alcohol is also used in witch hazel, liniments, collodions, tinctures of iodine and various other astringent lotions and antiseptics. Several types of aerosol-applied pharmaceuticals contain ethyl alcohol: i.e., medicated sprays for treatment of burns, cuts or insect bites and bandage sprays which form a plastic film over the area treated. It is an ingredient of a wide variety of ointment bases which serve as vehicles for medicaments. Some 2 million gallons of specially denatured alcohol went into these products during fiscal year 1960, making a total of over 4 million gallons for all externally used pharmaceuticals.

PHARMACEUTICALS FOR INTERNAL USE

Ethyl alcohol is employed as a vehicle for all manner of drugs and medicinal chemicals. It is the most frequently used liquid, other than water, in patent medicines as well as in medicines formulated according to doctors' prescriptions. Ethyl alcohol is often present in aerosol sprays for the nose and throat. Besides serving as a solvent in liquid pharmaceuticals, it is frequently used in compounding

pills by wet-granulation methods. Also, it serves as a solvent in tablet coating solutions based on materials such as polyvinylpyrrolidone.

GENERAL MEDICAL USE

Ethyl alcohol is important in preparing for surgical procedures. It is used to sterilize the skin area to be operated on and to sterilize surgeons' hands and gloves. Thermometers and other items are sterilized with alcohol. Patients are rubbed down with it to cleanse the skin and make them comfortable. In the laboratory, it is used to clean and dehydrate microscopic specimens and to prepare the staining solutions necessary for microscopic examination. Microscopic and anatomical specimens are frequently preserved in alcohol. Doctors sometimes have ethyl alcohol administered to their patients orally as a circulatory stimulant or appetizer, intravenously as an anesthetic or post-operative nutritive, and by injection into body tissues for the relief of intractable pain.

Cleaning Preparations

Specially denatured alcohol used in cleaning preparations totalled over 8 million gallons during fiscal year 1960. In addition, some portion of the 24.5 million gallons of proprietary and special industrial alcohol solvents manufactured that year also went into cleaning operations.

Ethyl alcohol is used in liquid detergents such as the following high-foaming composition (536):

	<i>Weight Per Cent</i>
Ammonium salt of sulfated Surfonic N-40 ¹	.50
Diethanolamide of lauric acid10
Ethyl alcohol25
Perfume	1
Water	14

¹ Jefferson Chemical Company Inc.

A quart of JAYSOL proprietary alcohol solvent in about a gallon of water makes an excellent window cleaning solution. Industrial glass cleaning compositions often contain ethyl and isopropyl alcohols, plus a surfactant. Various mixed solvent blends with ethyl alcohol are used to clean metal parts and molded plastics such as polystyrene.

JAYSOL ANHYDROUS
SDA-NJ-1771
PROPRIETARY SOLVENT
MIX & STORAGE TANK NO 2
CAPACITY 11,912 .81 W.G.
49.16 GALS. PER INCH

ALCOHOL
TANK NO 11
CAPACITY 11,912 .81 W.G.
49.16 GALS. PER INCH

JAYSOL S
SDA-N
PROPRIETARY
MIX & STORAGE
CAPACITY 11,912 .81 W.G.
49.16 GALS. PER INCH

Alcohol-containing special industrial solvents such as JAYSOL-S are used in the printing industry to clean type and machinery. Ethyl alcohol is used in formulations for cleaning scientific and optical instruments, jewelry, watches, cutlery and glassware.

Dry cleaning establishments use ethyl alcohol to help remove ink, tannin, perfume and various resinous stains from clothing. Ethyl alcohol is frequently an ingredient of transparent soaps based on materials such as coconut oil, castor oil, tallow and caustic soda.

Dyes, Inks and Stains

Ethyl alcohol has been used as a vehicle for coloring matter since the earliest times. It also had a role in the discovery of the first synthetic dye. In 1856, while attempting to synthesize quinine from aniline oil, the English chemist Perkin obtained a black, tarry substance. Dissolved in ethyl alcohol, this substance turned to a brilliant mauve color—the first of many coal-tar dyes to come.

Today, ethyl alcohol is used by the dye industry in several ways: (1) as a chemical raw material in the synthesis of dyes; (2) as a process solvent in the purification of dyes; and (3) as a solvent in dye solutions used by industry. The solubilities of various dyes in ethyl alcohol are listed below:

<i>Dye</i>	<i>Solubility in Ethyl Alcohol, Weight Per Cent</i>
Auramine O conc.	4.8
Metanile yellow	0.69
Chrysoidine Y	2.50
Chrysoidine R	5.23
Safranine	2.84
Methylene blue	0.099
Bismarck brown	3.81
Rhodamine B extra	12.50
Rhodamine 6 GNDX	14.40
Fuchsine	4.65
Nigrosine SSBS	2.30
Malachite green	13.80
Methyl violet crystals	soluble

Solutions of nitrocellulose, shellac or other resins in ethyl alcohol serve as vehicles for inks used in rotogravure and flexographic printing. Ethyl alcohol is also used in textile printing inks, in heat-sensitive inks, in aerosol-applied stencil inks and in intaglio inks for printing on metal foil. Proprietary alcohol solvents such as JAYSOL and non-hydrocarbon containing JAYSOL-S are widely used as thinners and cleaning fluids by the printing industry.

As a component of inks used in printing on cellulose ester surfaces such as Cellophane, ethyl alcohol exerts a slight solvent action on the printed surface. This enables the ink to penetrate the surface and solidify within the material, drying partly by absorption and partly by evaporation.

Ethyl alcohol is a commonly used solvent in spirit stains for dyeing wood. Such stains generally contain a little shellac as a binder to help fix the stain.

Adhesives

Ethyl alcohol is used in solvent blends for various resin-based adhesive compositions. In fiscal year 1960, this use accounted for 332,228 gallons of specially denatured alcohol.

In combination with esters, ketones and hydrocarbons, ethyl alcohol is used as a solvent for thermoplastic adhesives based on polyvinyl acetate, polyvinyl butyral and polyvinyl alcohol. A typical application for these vinyls is in pressure sensitive tape. Cellulose derivatives form another group of thermoplastic adhesives in which ethyl alcohol is used. The most important of these is nitrocellulose, however, ethylcellulose and mixed cellulose esters are also used. The technology of nitrocellulose adhesives closely parallels the technology used in formulating lacquers based on the same material. Household cements and binders for shoe soles are typical nitrocellulose adhesive applications.

Of the thermosetting adhesive resins, urea-formaldehydes and phenolics may employ ethyl alcohol as a solvent. A typical application is in manufacturing laminated products such as plywood.

Ethyl alcohol is not used in adhesives of the rubber-base type or in water soluble glues.

Explosives

Ethyl alcohol is important in the manufacture of explosives, especially smokeless powder. During fiscal year 1960, consumption for this purpose totalled 654,114 gallons of new alcohol. The alcohol is recovered during the manufacturing process and in 1960 over 4.7 million gallons were recovered and reused.

In smokeless powder manufacture, nitrocellulose is solubilized to a concentrated sol and forced through small holes to form the grains of powder. Ether-alcohol mixtures are commonly used as the solubilizing media although acetone replaced ether in some processes during World War II.

Extraction and Crystallization

The wide solvent powers of ethyl alcohol recommend its use as an extracting agent for many natural products. It has been patented for use in extracting odorant principles and essential oils such as lemon oil and oil of wintergreen. Many different alkaloids and related substances may be obtained by ethyl alcohol extraction. These include codeine, strychnine, lobeline, brucine, quinine, cinchonine, emetine, ephedrine, scopolamine, hyoscyanine, duboisine, atropine, eserine, hydrastine, aconitine, pilocarpine, sparteine, colchicine, arecoline, nicotine and caffeine. Frequently the salts are extracted instead of the free base because of their increased solubility in ethyl alcohol. Plant principles such as witch hazel, bay oil and pyrethrum also are extracted by ethyl alcohol. Ethyl alcohol is used in processing ripe fruits to obtain pectin, an important ingredient of jellies. Miscellaneous applications include extraction to produce vitamin-free casein, zein from corn gluten, lanolin, benzaldehyde, trinitrotoluene, refined montan wax and peanut and mowrah oils.

Ethyl alcohol is used for the purification of many drugs and fine chemicals by recrystallization. These include glandular products, vitamins, aconite, sulfonal, guaiacol, monobrominated camphor, *o*-toluenesulfonamide, phenyl salicylate, terpin hydrate, heliotropin, beta-naphthol benzoate, and oxalic acid.

No attempt has been made here to survey the extensive patent literature pertaining to the use of ethyl alcohol as an extracting and crystallization agent.

Aerosol Products

An ever-increasing number of aerosol-dispensed products are being put on the market each year. Ethyl alcohol is one of the most important solvents used in such products. Virtually all types of liquid cosmetics are now dispensed from pressurized containers, e.g. hair lacquers, face lotions, perfumes, sun-tan lotions and anti-perspirants. Many alcohol-containing pharmaceuticals, cleaning preparations and space deodorants are also available in aerosol form. Both clear and pigmented coatings based on nitrocellulose, shellac and other materials are packaged as aerosols for specialized uses.

The problems involved in aerosol packaging are very complex and the cost of delivering the active ingredients to their destination can be quite high compared with other methods. But aerosols have more than enough advantages to compensate for these drawbacks. Products can be quickly and easily applied directly to the location desired in their most effective state of dispersion. Sprays can range anywhere from a very fine mist to coarse droplets. Furthermore, the exact quantity of product wanted can be used, with instant control of spray starting and stopping. The sealed container eliminates the possibility of product contamination.

Ethyl alcohol is miscible with all the commonly used propellents. Most of these are chloro- and fluoro-substituted derivatives of methane and ethane. Among the most widely used are dichlorodifluoromethane (propellent 12) and trichlorofluoromethane (propellent 11).

One problem that has arisen in using ethyl alcohol with propellent 11 is the development of acidity, odor distortion and container corrosion. This is caused by the interaction of the alcohol and propellent to form acetaldehyde and hydrogen chloride (537). Bower and Long have recently (1961) shown, however, that nitromethane acts as a stabilizer and effectively inhibits this reaction (538). The nitromethane has no toxic effects and is best added to alcohol-based formulations as a 0.3% solution in propellent 11.

Much research has been done on the subject of ethyl alcohol in aerosols and a number of books exist which discuss this subject (539-550 and others).

Other Solvent Applications

Ethyl alcohol is used as a solvent in the manufacture of various plastics—over 2 million gallons were used for this purpose during

fiscal year 1960. Another use is in the production of plastic sheeting. It is also used as a vehicle for the antioxidants and light-absorbing chemicals which are sometimes added to plastics and coating compositions. Some photographic film and emulsions are manufactured with the help of ethyl alcohol. It is also used in photographic developers and as a drying agent for negatives, prints and plates. Ethyl alcohol is often used in photoengraving and rotogravure solutions and dyes.

Ethyl alcohol performs as a solvent in many spray- and wick-type deodorants for homes and buildings. It is also used in disinfectants, insecticides, fungicides and insect repellents. It is used as an ingredient of soldering fluxes and in compositions for etching steel, copper, magnesium and other metals. Certain polishes and shoe dressings contain ethyl alcohol. It is used in processing food products and is a vehicle for sorbic acid and other preservatives.

During fiscal year 1960, three-quarters of a million gallons of new alcohol were used in processing petroleum oils. This alcohol was recovered and reused many times over; during that period over 7 million gallons of recovered alcohol were used. Ethyl alcohol is also used in processing rosin and other materials.

The various formulations given in this chapter are only typical ones. Because of the remarkable compatibility of ethyl alcohol with other solvents, the number of formulations possible are legion. Many of these have been collected into formularies, pharmacopoeia, and similar books (507, 539, 551-556 and others).

MISCELLANEOUS APPLICATIONS

The industrial utilization of ethyl alcohol is conveniently divided into chemical uses and solvent uses (Figure 8). There are, however, many other applications of ethyl alcohol which do not fit these broad classifications. Several of these are noted in this chapter.

Motor Fuel

The use of ethyl alcohol as a fuel for spark-ignited internal combustion engines and to a lesser extent in diesel type engines (557) has been the subject of many papers, some books and even a few laws of the land. Most of the reasons for this interest in alcohol for power are economic in nature. Countries without a national source of petroleum have a continuing interest in agricultural-derived motor fuels and other countries in times of over production of carbohydrate crops turn to fuel alcohol as a possible outlet. Some countries have even gone to the extent of passing laws requiring alcohol to be blended with gasoline. A brief history and many references up to 1937 are given by Ellis in "The Chemistry of Petroleum Derivatives" (96).

Since 1937 there has been a small but definite interest in ethyl alcohol as a motor fuel or as an additive to gasoline or similar hydrocarbon fuels. One of the blends (Agrol) proposed for use in the United States contained 78% ethyl alcohol, 7% other alcohols from American farm crops and 15% fuels produced from coal (558). The ethyl alcohol was to be of fermentation origin and preferably from a surplus farm crop.

World War II revived interest in industrial alcohol as a motor fuel. In 1943 the Department of Agriculture published a bulletin on industrial alcohol which included data on its behavior in the internal combustion engine and on its use as a motor fuel both in the United States and abroad (36). Current use in this country is restricted to rockets, guided missiles, torpedo propulsion, special fuels for racing cars, small stoves, chafing dishes, cigar lighters and in lamps using Welsbach mantles, in which ethyl alcohol produces 3.5 times as much light as kerosene fuel. Specially denatured alcohol used as a fuel totalled 528,536 gallons during fiscal year 1960. This amount does

not include any proprietary alcohol solvents used as fuels during that period.

Other countries have a greater interest than the United States in motor alcohol (559-562). This is reflected in their laws and in the various sources of fermentation alcohol. Almost anything which can be fermented to ethyl alcohol has been promoted at one time or another. These include such widely different materials as Douglas fir tar (563), agricultural residues, corn, Jerusalem artichokes (558), and water hyacinth (564).

Dehydration of Nitrocellulose

A considerable amount of ethyl alcohol is used in the dehydration of nitrocellulose. Over 4 million gallons of new alcohol were used for this purpose during fiscal year 1960. In the dehydration process, most of the alcohol is recovered and reused; during 1960 recovered alcohol totalled over 14 million gallons.

The nitrocellulose manufacturing process begins with cellulose, which is derived from cotton linters or wood pulp. Purified cellulose is nitrated with a mixture of nitric and sulfuric acids, then is washed to remove retained acid and unstable reaction products. The nitrocellulose then undergoes a digestion stage to reduce its viscosity. After additional washings, the slurry of nitrocellulose in water is ready for dehydration.

Most of the water is allowed to drain out, then more water is forced out with presses. The remaining water is then displaced with ethyl alcohol, which is pumped through the nitrocellulose under pressure. The alcohol-wet compressed blocks of nitrocellulose are then broken up to loosen the fibers so that they will be accessible to the solvents used in compounding lacquers, plastics and other products.

Most nitrocellulose is sold wet with 30% by weight of ethyl alcohol, generally S.D.A. 2-B. The quantity of alcohol present in the nitrocellulose must be taken into account when compounding lacquers and other products. Other damping media sometimes used for commercial nitrocellulose are isopropyl alcohol, butyl alcohol or water.

Ethyl alcohol is also used in the dehydration of sodium hydrosulfite, an important bleaching and reducing agent.

Antifreeze

The use of ethyl alcohol as a general antifreeze for automobiles at one time utilized a large fraction of the total production. Currently ethyl alcohol is not used extensively for this purpose but it has many other specialized antifreeze applications. It is used as a coolant medium in freezing cabinets and in air conditioning systems as a substitute for brine. It will prevent icing of carburetors of internal combustion engines and it may be used for the de-icing of airplane propellers. Ethyl alcohol is used to prevent the freezing of liquids in gauges, meters, gas lines, sewage systems and toilets in unheated buildings. Alcohol added to compressed gases when they expand through a reducing valve will prevent the freezing of any water present.

Lithium chromate has been patented as a corrosion inhibitor for ethyl alcohol based antifreeze solutions (565).

Other Uses

A discussion of the miscellaneous uses of ethyl alcohol could fill a book. Only a few of these uses will be noted here but they will serve to illustrate the general usefulness of ethyl alcohol.

Foam inhibition of hydrocarbon oils (566).

Chemical control and overseasoning of, and natural inoculation with, the soil-borne viruses of wheat and oats (567).

As a medium for anode polarography (568).

Control of spoilage of purple passion fruits (*Passiflora edulis*) caused by species of *Aspergillus*, *Fusarium*, *Rhizopus* and *Penicillium* (569).

In feed of ruminants (570).

Indicating liquid in gauges, compasses and spirit levels.

Working liquid in low-temperature thermometers, door checks and hydraulic fluids.

Cooling agent with solid carbon dioxide.

Component of household lubricating oil.

Carrier or vehicle for cutting oils.

Vehicle for gum inhibitors for gasoline.

Vehicle for digestive ferments.

Component of embalming fluids and related products.

Reaction Medium

When a chemist wishes to carry out a chemical reaction in a solvent other than water he instinctively thinks first of ethyl alcohol. This is reflected in the literature and can best be illustrated by taking a typical year (1957) and noting the references to this use which appear in "Chemical Abstracts."

Reaction between aniline and methyl iodide (571).

Metal-ion catalysis and polarity of environment in the aerobic oxidation of unsaturated fatty acids (572).

Reaction of 1,2-dichloro-1,1,3,3,3-pentafluoropropane with ethanolic alkali (573).

Action of sulfuric acid solution in ethanol on *d*-3-carene (574).

Solvent effect on the acid decomposition of 1,3,5-trinitroso-1,3,5-triazocyclohexane (575).

Conductance of lithium nitrate solutions in ethyl alcohol and ethyl alcohol-water mixtures at 25°C. (576).

The application of Taft's equation to polar effects in solvolyses (577).

The acidic solvolysis of organosilicon hydrides (578).

Effect of the nature of the solvent on the process of catalytic hydrogenation of an unsaturated compound by palladium on calcium carbonate (579).

Effect of solvent on the rates of solvolysis of 1,2-dichloro-2-methylpropane and of 3-chloro-2-methylpropene (580).

Action of *N,N*-dichlorobenzenesulfonamide on alcoholic solution of piperidine (581).

Action of *N,N*-dibromobenzenesulfonamide on solutions of piperidine in methyl and ethyl alcohols (582).

Solvolysis of *cis*- and *trans*-2-*tert*-butylcyclohexyl *p*-toluenesulfonate (583).

Solvolysis of 6-oxocyclodecyl *p*-toluenesulfonate and *p*-bromobenzenesulfonate (584).

Solvolytic reactivities of some 7-chloronorbornane derivatives (585).

Acyl cleavages with diazomethane (586).

Activation of alcoholyses with diazomethane (587).

Hydrogenation of gaseous olefins under pressure (588).

Copper complexes in 75% (vol/vol) ethanol-water (589).

The effect of solvent on a simple ion-dipole reaction (590).

Ionization of *para*-substituted 3-methylbenzoic acid (591).
Effect of formaldehyde and organic solvents on the decomposition reaction of hexamine by acid (592).
Interaction between sulfur dioxide and polar molecules (593).
The heat capacity of activation for the ethanolysis of methyl *p*-nitrobenzenesulfonate (594).
Decomposition of benzoyl peroxide in alcohols (595).
The kinetics of solvolysis of acyl esters of salicylic acid (596).
Reaction between benzyl chloride and potassium cyanide in 80% ethyl alcohol (597).
Dissociation constants of 2,4-dinitrophenol, chloracetic acid and propionic acid in 20% ethyl alcohol (598).
Kinetics of the solvolysis of alkyl borate (599).

PHYSICAL PROPERTIES

Probably no other organic compound has been so extensively studied as ethyl alcohol in respect to its physical properties, both alone and in solution with water and with other organic compounds. Its ability to dissolve many inorganic compounds has given an even greater scope to the investigations. There will be reported in this chapter only the principal physical properties of ethyl alcohol, ethyl alcohol-water mixtures and other binary and ternary mixtures of ethyl alcohol. The coverage is selective rather than comprehensive.

In 1913 Osborne, McKelvey and Bearce published a very complete monograph on the density and expansion of pure ethyl alcohol and its mixtures with water (242). Since that time numerous compilations of these and other data have been made. The books include "The International Critical Tables of Numerical Data, Physics, Chemistry and Technology" (640), "Organic Solvents" (600), "Physico-Chemical Constants of Pure Organic Compounds" (601), and various handbooks. Reid and Smith (1951) (602), and Papini and Cuomo (1956) (603) have made critical studies of the thermodynamic properties of ethyl alcohol.

Selected physical properties of pure ethanol are given in Table XVIII. Tables XIX to XXII contain data on mixtures of ethyl alcohol with water and other substances.

Pure Ethyl Alcohol

Table XVIII

SELECTED PHYSICAL PROPERTIES OF PURE ETHANOL

Molecular weight	46.07
Boiling point, 760 mm, °C	78.3
Freezing point, °C	-114.49
Critical temperature, °C	243.1
Critical pressure, mm Hg	47,850
Index of refraction, n_D^{20}	1.36139
Specific gravity, 20/20°C	0.7905
Pounds/gallon, 20°C	6.6
Vapor pressure, mm Hg, 25°C	59.02
Heat of vaporization, cal/g	204
P.t.u./lb	367
Heat of combustion, cal/g	7,092.9
B.t.u./lb	12,767

Table XVIII (continued)

SELECTED PHYSICAL PROPERTIES OF PURE ETHANOL

Specific heat, Cp, 25°C	0.588
Dielectric constant, 20°C	25.00
Viscosity, centipoises, 25°C	1.078
Surface tension, dynes/cm, 20°C	22.28
Flash point, Tag. open cup, °F	65
Boiling point, °C (760 mm)	78.27 (604)
	78.3 (605-607)
	78.32 (608)
	78.325 (600, 609)
	78.33 (610)
	78.34 (611)
	78.35 (612)
dt/dp, °C at 760 mm	0.0334 (609)
	0.03286 (604)
Freezing point, °C	-114.15 (601)
	-114.49 (604)
Melting point, °C	-110.5 (608)
Critical temp., °C	243.1 (613)
Critical pressure, mm Hg	47,850 (613)
Atms	63.11 (613)
Critical volume, liters/g mole	0.1669 (603)

Density, g/ml	Temp. °C	dt
	0	0.806306 (614)
	5	0.80209 (615)
	10	0.79787 (615)
	15	0.79360 (608)
	20	0.78934 (616)
	25	0.78505 (604, 617)
	25	0.78506 (242)
	25	0.785063 (614)
	25	0.78508 (610)
	25	0.78512 (606)
	30	0.78075 (242)
	35	0.77641 (242)
	40	0.77203 (242)
	50	0.763137 (614)

$$d = 0.78506 - 0.0008591(t - 25) - 0.00000056(t - 25)^2 - 0.000000005(t - 25)^3 \quad (242)$$

See also (618)

Index of refraction	Temp. °C	n _D
	20	1.36152 (605)
	20	1.36155 (604)
	25	1.35936 (606)
	25	1.359408 (619)
	25	1.35941 (600, 604)
dn/dt		0.0004 (620)
20°/G°		1.3700 (620)
20°/F		1.3666 (620)
20°/C		1.3605 (620)

Table XVIII (continued)
SELECTED PHYSICAL PROPERTIES OF PURE ETHANOL

Vapor pressure	Temp. °C	mm Hg (610)
	0.000	11.95
	25.000	59.02
	34.988	103.03
	44.994	172.95
	50.000	220.94
	54.988	279.79
	65.000	438.04
	78.553	766.71
Calcd.	78.328	760.00

$$\text{Log } P_{\text{mm}} = 8.11576 - [1595.76/(t_c + 226.50)] \quad (610)$$

See also (621)

Temp. °C	mm Hg (608)
-31.5	1
-12.0	5
- 2.3	10
+ 8.0	20
19.0	40
26.0	60
34.9	100
48.4	200
63.5	400
78.3	760

See also (601, 607, 613, 622)

Surface tension	Temp. °C	Dynes/cm
	15	22.76 (623)
	20	22.28 (624)
	20	22.32 (623)
	20	22.8 (625)
	25	21.85 (626)

Dielectric constant	Temp. °C	E
	0	27.88 (627)
	10	26.41 (627)
	20	25.00 (627)
	25	24.14 (626)
	25	24.25 (627)
	35	22.79 (627)
	45	21.53 (627)
	55	20.21 (627)

Dipole moment, D, 30°C, benzene	1.66 (611)
	1.70 (628)
	1.74 (629, 630)
gas value	1.67 (631)
	1.69 (632)
	1.70 (633)

Table XVIII (continued)

SELECTED PHYSICAL PROPERTIES OF PURE ETHANOL

Viscosity	Temp. °C	Centipoises (634)
	-100	.47
	-80	18.1
	-60	8.7
	-50	6.4
	-40	4.79
	-30	3.65
	-20	2.38
	-10	2.23
	0	1.78
	+10	1.46
	20	1.19
	30	1.00
	40	0.825
	50	0.701
	60	0.591
	80	0.435
	100	0.326
	120	0.248
	140	0.190

See also (601, 635)

Specific heat	Temp. °C	Specific Heat, Cal/g/°C
	-73.1	0.468 (636)
	-33.1	0.507 (636)
	+ 1.9	0.543 (636)
	16.9	0.572 (636)
	24.9	0.588 (636)
	30.0	0.603 (637)
	35.0	0.614 (637)
	40.0	0.633 (637)
	45.0	0.653 (637)
	50.0	0.669 (637)
	55.0	0.688 (637)
	60.0	0.705 (637)
	65.0	0.732 (637)
	70.0	0.753 (637)

See also (638)

Heat Capacity, Cp Liquid at 25°C, cal/g °C	0.581 (639)
Cp Vapor 90°C, 1 atm, cal/g °C	0.406 (639)
Cv Vapor 90°C, 1 atm, cal/g °C	0.359 (639)
Cp = 19.02967 - 0.004812T + 0.0000913T ²	(603)

Table XVIII (continued)

SELECTED PHYSICAL PROPERTIES OF PURE ETHANOL

Thermodynamic Properties (602)

Temp., °F	Pressure, psia	Specific Volume, cu ft/lb		Enthalpy, B.t.u./lb		Entropy, B.t.u./lb/°F	
		Sat. Liq.	Sat. Vap.	Sat. Liq.	Sat. Vap.	Sat. Liq.	Sat. Vap.
32	0.238	0.01986	475.5	0.0	407.2	0.0	0.8231
40	0.319	0.01996	360.5	4.4	409.7	0.0089	0.8200
50	0.459	0.02007	255.3	9.8	412.8	0.0196	0.8103
60	0.647	0.02020	184.3	15.4	415.9	0.0304	0.8010
70	0.910	0.02033	135.5	21.0	418.9	0.0411	0.7933
80	1.26	0.02045	98.8	26.9	422.0	0.0521	0.7842
90	1.71	0.02057	73.3	32.9	425.1	0.0631	0.7766
100	2.30	0.02070	55.3	39.0	428.0	0.0741	0.7691

See also (603)

Heat of vaporization	Temp., °C	cal/g
	20	217.9 (640)
	40	215.0 (640)
	50	211.9 (641)
	60	210.2 (640)
	78.3	204.3 (608)
	90	195.7 (641)
	100	193.5 (640)
	110	185.9 (641)
	120	181.6 (640)

$$Q = 9.290 + 0.02593T - 0.0000649T^2 \quad (0^\circ \text{ to } 200^\circ\text{C}) \quad (603)$$

Heat of Combustion, 25°C (C _p), cal/g	7092.9 (642)
kcal/mole	328
Latent heat of fusion, cal/g	24.9 (608)
Free energy of formation, ΔF at 25°C, kcal/mole	-40.2 (639)
Heat of formation, liquid, ΔH at 25°C, kcal/mole	-64.7 (639)
Coefficient of cubic expansion, 20°C	0.0018 (608)
Electrical conductivity, 25°C, reciprocal ohms	1.35 x 10 ⁻⁹ (608)
Explosive mixture with air, 20°C, vol % (608)	
Upper Limit	19
Lower Limit	3.3

See also (643)

Flash point, closed cup	57°F; 14°C (608)
Fire point	59°F; 15°C
Autoignition temp., °C	390-430 (608)
Heat of solution in water at 13°C, kcal/mole solute	2.54 (639)

See also (622)

DATA ON LESS COMMON PHYSICAL PROPERTIES

Absorption of decimeter waves (644).

Crystalline ethyl alcohol at -180°C, X-ray analysis (645).

Density, Molecular structure and (646).

Dielectric polarization of ethyl alcohol adsorbed on silica gel (647).

Table XVIII (continued)

SELECTED PHYSICAL PROPERTIES OF PURE ETHANOL

Dielectric properties of liquid ethyl alcohol from room temperature to -160°C (648).

Entropy from molecular data and the equilibrium in the hydration of ethylene (649).

Heat capacity, gas imperfection, infrared spectra, and internal rotation barriers (283).

—of evaporation; molecular structure and (650).

—of solution of ammonia at 25°C (651).

—transfer (J_H) and the mass transfer (J_D) factors for air drying (652).

—of vaporization as a function of specific values of phases (653).

—of vaporization, equation for calculating (654).

—of vaporization, hydrogen-bond contribution (655).

Infrared measurements of the association of ethyl alcohol in carbon tetrachloride (656).

Ionization potential (657, 658).

Light scattering, compound, the influence of temperature (659).

Mass spectrum (303).

Molecular diameter (660).

Nuclear magnetic resonance spectra, double-quantum transitions (661).

Nuclear magnetic resonance studies of hydrogen bonding (662).

Orientation of polar molecules around ethyl alcohol molecules, structural coefficients of the internal field produced (663).

Polarization in certain ethers (664).

Refractive index-temperature data at 10° , 15° , 20° , 25° , and 30°C (665).

Refractive indices at high pressures (666).

Solubilities of sodium chloride, sodium bromide, sodium iodide, potassium chloride, potassium bromide and potassium iodide (626).

Specific heat at constant pressure and cohesion (667).

Specific heat of solutions of salts (668).

Surface energy and cohesion as a function of temperature (669).

Thermal conductivity (670).

Table XVIII (continued)

SELECTED PHYSICAL PROPERTIES OF PURE ETHANOL

Ultrasonic absorption and the theory of the equation of state at ordinary temperatures (671).

Ultrasonic waves in ethyl alcohol, structural absorption (672).

Ultrasonic waves in superheated vapors, the velocities (673).

Vaporization into quiet humid air (674).

Viscosity up to 190°C, measurement (635).

Volume of ethyl alcohol as a function of pressure and temperature (675).

Zero and critical density (618).

Ethyl Alcohol-Water Mixtures

Table XIX

**SELECTED PHYSICAL PROPERTIES OF
ETHYL ALCOHOL-WATER MIXTURES**

Boiling point, azeotrope, °C, 760 mm Hg	78.15
Azeotrope composition: wt % alcohol	95.57 (495)
vol % alcohol	97.25
mole % alcohol	89.43

Boiling point at various concentrations, °C, 760 mm Hg (640)

Wt % Alcohol	Boiling point
0.000	100
4.96	95.1
11.86	90.5
16.14	88.6
22.13	86.5
38.97	83.2
52.29	81.7
63.03	80.8
71.88	80.0
79.33	79.4
88.48	78.7
95.60 (95.57)	78.15
95.84	78.2
100.00	78.3

Boiling points of ethyl alcohol-water mixtures, °C (676)

Boiling point	Wt % alcohol in	
	Liquid	Vapor
78.2	91	92
78.4	85	89
78.6	82	88
78.8	80	87

Table XIX (continued)
SELECTED PHYSICAL PROPERTIES OF
ETHYL ALCOHOL-WATER MIXTURES

Boiling point	Wt % alcohol in	
	Liquid	Vapor
79.0.....	78	86
80.0.....	67	83
82.0.....	41	79
84.0.....	27	76
86.0.....	20	72
88.0.....	15	68
90.0.....	10	61
92.0.....	8	53
94.0.....	5	44
96.0.....	3	33
98.0.....	1	19
100.0.....	0	0

See also (677)

Freezing points at various concentrations (678)

Wt % Alcohol	Freezing Point, °C
5	—2.0
10	—4.5
15	—7.2
20	—11.0
25	—15.8
30	—20.5
40	—30.5
50	—38.0
60	—43.5
70	—50.5
80	—67.0
85	—87.5
90	—113.0
92.5.....	—125.0 Eutectic
95	—120.0
100	—114.5

Index of refraction at various concentrations, n_{D}^{21} (640)

Wt % Alcohol	n
0.00.....	1.33336
6.00.....	.33721
17.56.....	.34581
22.11.....	.34919
26.06.....	.35162
29.87.....	.35443

Table XIX (continued)
SELECTED PHYSICAL PROPERTIES OF
ETHYL ALCOHOL-WATER MIXTURES

Wt % Alcohol	n
38.98.....	.35883
56.09.....	.36408
63.01.....	.36535
72.50.....	.36630
91.09.....	.36574
100.00.....	.36316

Specific gravity at various concentrations, 20°/20°C (495)

Wt % Alcohol	Sp. Gr.
0.0.....	1.0000
5.0.....	.9911
10.0.....	.9836
15.0.....	.9768
20.0.....	.9703
30.0.....	.9555
40.0.....	.9368
50.0.....	.9153
60.0.....	.8926
70.0.....	.8691
80.0.....	.8447
85.0.....	.8322
90.0.....	.8192
95.0.....	.8054
100.0.....	.7905

Specific gravity (t/20°C), and weight per gallon (lb/gal), at various temperatures (°C) of 95% ethyl alcohol. (495)

Temp.	Sp. Gr.	Lb/gal
-20.....	0.8461	7.04
15.....	0.8417	7.01
10.....	0.8373	6.97
- 5.....	0.8329	6.93
0.....	0.8285	6.90
+ 5.....	0.8241	6.86
10.....	0.8197	6.82
15.....	0.8153	6.79
20.....	0.8109	6.75
25.....	0.8065	6.71
30.....	0.8021	6.68
35.....	0.7977	6.64
40.....	0.7933	6.60
55.....	0.7801	6.49

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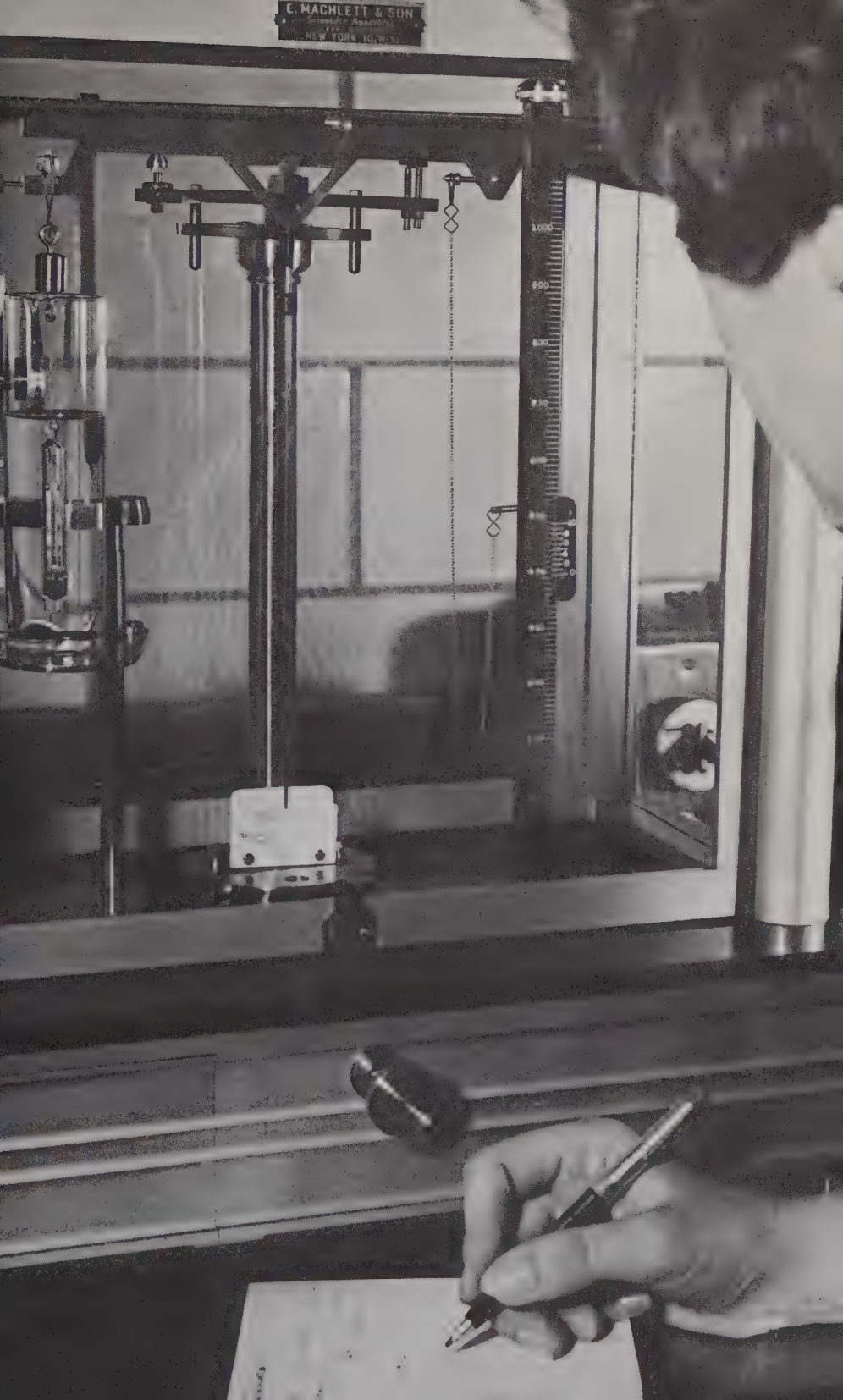


Table XIX (continued)
SELECTED PHYSICAL PROPERTIES OF
ETHYL ALCOHOL-WATER MIXTURES

Specific gravity (t/4°C) (640)

Weight % Ethyl Alcohol	10°C	20°C	30°C	40°C
0	0.99973	0.99823	0.99568	0.99225
10	0.98393	0.98187	0.97875	0.97685
20	0.97252	0.96864	0.96639	0.95856
30	0.95977	0.95382	0.94741	0.94055
40	0.94238	0.93518	0.92770	0.91992
50	0.92126	0.91384	0.90580	0.89750
60	0.89927	0.89113	0.88278	0.87417
70	0.87602	0.86766	0.85908	0.85025
80	0.85197	0.84344	0.83473	0.82578
90	0.82654	0.81797	0.80922	0.80028
100	0.79784	0.78934	0.78075	0.77203

Specific gravity of ethyl alcohol-water solutions

Weight % Ethyl Alcohol	10°/10°C	20°/20°C	30°/30°C	40°/40°C
0	0.99973	0.99823	0.99567	0.99224
10	0.98420	0.98361	0.98301	0.98449
20	0.97278	0.97036	0.97059	0.96606
30	0.96003	0.95551	0.95153	0.94791
40	0.94263	0.93684	0.93173	0.92714
50	0.92151	0.91548	0.90974	0.98263
60	0.89951	0.89271	0.88662	0.88101
70	0.87626	0.86920	0.86282	0.85690
80	0.85220	0.84494	0.83836	0.83224
90	0.82676	0.81942	0.81274	0.80654
100	0.79805	0.79074	0.78415	0.77807

Specific Heat at various temperatures (640)

Ethyl Alcohol, Mole %	Specific Heats, Cal/g°C		
	At 3°C (±0.5%)	At 23°C (±0.5%)	At 41°C (±1%)
0.0	1.006	0.9991	0.9972
2.02	1.031	1.012	1.013
4.16	1.046	1.021	1.025
6.46	1.050	1.030	1.032
8.91	1.042	1.033	1.033
11.5	1.023	1.027	1.027
14.4	1.000	1.013	1.017
20.7	0.9377	0.9740	0.9814
28.1	0.8653	0.9190	0.9312
37.0	0.8044	0.8572	0.8732
47.7	0.7482	0.7953	0.8132
61.0	0.6694	0.7263	0.7482
77.9	0.6135	0.6594	0.6835
100	0.5406	0.5774	0.6214

Table XIX (continued)

SELECTED PHYSICAL PROPERTIES OF ETHYL ALCOHOL-WATER MIXTURES

Thermal Conductivity at 68°F (679)

Ethyl Alcohol, Wt %	k
100.....	0.105
80.....	0.137
60.....	0.176
40.....	0.224
20.....	0.281

k = B.t.u./ (hr) (sq ft) (°F/ft)

OTHER DATA ON THE ETHYL ALCOHOL-WATER SYSTEM

Aqueous ethyl alcohol, adsorption from, on silicic acid gel (680).

- compression (681).
- thermal conductivity (682, 683).
- ultrasonic absorption (684, 685).

Condensation of aqueous-alcoholic vapors, heat transfer calculation of the coefficient (686).

Densities in the system ethyl alcohol-water, empirical formulas for calculation of, at various temperatures (687).

Distribution of ethyl alcohol between water and benzene (688).

Ethyl alcohol-water mixtures, dependence of concentration on chemical exchange (689).

- concentration dependence of chemical exchange and NMR multiplet structure (690).
- magnetic susceptibility (691).
- surface tension (692).

Heats of solution of halides, sulfuric acid, oxalic acid, sodium hydroxide and urea in ethyl alcohol-water mixtures (693).

Heat transfer rate function for the system ethyl alcohol-water (694).

Linear density-temperature relationship and a three-constant log d and concentration relationship at constant temperature, constants (695).

Liquid-vapor equilibria of ethyl alcohol-water mixtures between 120° and 180°C (696).

- at high pressures (697).
- at one atmosphere (698).

Molar volumes in dilute aqueous solution, apparent (699).

1-Octene distribution in ethyl alcohol-water at 0° and 25°C (700).

Table XIX (continued)
SELECTED PHYSICAL PROPERTIES OF
ETHYL ALCOHOL-WATER MIXTURES

Specific heat (C_V) at constant volume, a new method for determining (701).

Thermodynamics of dilute ethyl alcohol-water mixtures—vapor pressure activities, heat of solution (622).

2,2,4-Trichloropentane, distribution between ethyl alcohol and water at 0° and 25°C (700).

Vapor-liquid equilibria, salt effects in aqueous ethyl alcohol (702, 703).

Other Binary Mixtures

Table XX
SELECTED PHYSICAL PROPERTIES OF
OTHER BINARY MIXTURES

Apparent specific gravity of ethyl alcohol-ethyl ether mixtures at 20°C (495)

Ethyl Alcohol Weight %	Specific Gravity, 20°/20°C
0.....	0.7147
5.....	0.7195
10.....	0.7241
20.....	0.7332
30.....	0.7414
40.....	0.7492
50.....	0.7568
60.....	0.7641
70.....	0.7715
80.....	0.7785
90.....	0.7849
95.....	0.7880
100.....	0.7910

Composition of various binary azeotropes (639)

Compound	Wt % Ethyl Alcohol	Wt % Compound	Azeotrope B.P. °C
Benzene	32.4	67.6	68.3
1-Bromopropane	16.3	83.7	63.6
2-Bromopropane	11.5	88.5	55.5
Carbon disulfide	9	91	42.4
Carbon tetrachloride	15.8	84.2	64.9
Chloroform	7.0	93.0	59.4

Table XX (continued)
SELECTED PHYSICAL PROPERTIES OF
OTHER BINARY MIXTURES

Compound	Wt % Ethyl Alcohol	Wt % Compound	Azeotrope B.P.°C
1-Chloropropane	6	94	46.7
2-Chloropropane	2.8	97.2	36.6
Cyclohexane	30.5	69.5	64.9
Cyclopentane	7.5	92.5	44.7
2,5-Dimethylhexane	59	41	73.6
Ethyl Acetate	31	69	71.8
Ethyl propionate	75	25	78.0
n-heptane	49	51	70.9
n-hexane	21	79	58.6
Isoprene	3	97	32.7
Methyl acetate	3	97	56.9
Methyl carbonate	45	55	73.5
Methyl ethyl ketone	34	66	74.8
Methyl propionate	33	67	72.0
Octane	78	22	77.0
Pentane	5	95	34.3
Propyl acetate	85	15	78.2
Toluene	68	32	76.7
Trichloroethylene	27	73	70.9

DATA ON LESS COMMON BINARY SYSTEMS

Electrolytes, effect of, on ethyl alcohol-acetone and ethyl alcohol-carbon disulfide mixtures (703).

Ethyl alcohol-acetic acid, equilibrium curve from the curve of the liquid-phase composition (704).

—acetone solutions, refractive indices and bubble points at 760 mm (705).

—benzene mixtures at 20°C, surface tension (625).

—benzene, vapor-liquid equilibria (706, 707).

—carbon tetrachloride at 25°C, diffusion in the system (708).

—carbon tetrachloride, thermodynamic properties of the system (709).

—chloroform, experimental work on the vapor-liquid system (710).

—chloroform mixtures at 35°, 45°, and 55°C, vapor-liquid equilibria (621).

—cyclohexane, heats of mixing (711).

—cyclohexane mixtures, relationships among the temperature, pressure, and composition changes (694).

- dioxane mixtures, properties versus composition (712).
 - ethyl acetate system, heats of mixing and excess thermodynamic properties at 25°C (713).
 - ethyl acetate mixtures, vapor-liquid equilibria (606).
 - isooctane (2,2,4-trimethylpentane), vapor-liquid equilibria and densities of the system between 0° and 50°C (614).
 - methylcyclohexane mixtures, vapor-liquid equilibria (617).
 - toluene, heats of mixing (711).
 - toluene mixtures, vapor-liquid equilibria (610, 706).
- Thermal conductivity of various binary solutions of ethyl alcohol (683).
- Vapor-liquid equilibria for binary systems of ethyl alcohol with alcohols and ketones (714).
- Volume curves, excess, based on density measurements of ethyl alcohol with toluene, chlorobenzene and bromobenzene at 25° and 30°C (715).

Ternary Mixtures

Table XXI
SELECTED PHYSICAL PROPERTIES OF
TERNARY MIXTURES

Composition of various ternary azeotropes (639)

Compound	Wt % Ethyl Alcohol	Wt % Water	Wt % Compound	Azeotrope B.P.°C
Acetal	27.6	11.4	61	77.8
Benzene	18.5	7.5	74	64.85
Bromodichloromethane	22.6	7.4	70	72.0
1-Bromo-2-methylpropane ..	27	8	65	69.5
1-Bromopropane	12	5	83	60.0
2-Bromopropane	4	1	95	43.3
Chloroform	4	3.5	92.5	55.4
1-Chloro-2-methylpropane ..	13	4.5	82.5	58.6
Cyclohexene	20	7	73	64.1
1,2-Dichloroethane	17	5	78	66.7
cis-1,2-Dichloroethylene	6.6	2.9	90.5	53.8
trans-1,2-Dichloroethylene ..	4.4	1.1	94.5	44.4
Ethyl acetate	8.4	9.0	82.6	70.2
Trichloroethylene	16.1	5.5	78.4	67.0
Triethylamine	13	9	78	74.7

DATA ON OTHER TERNARY MIXTURES

Ethyl alcohol-benzene-cyclohexane, heats of mixing (711).

- benzene-*n*-heptane ternary system, vapor-liquid equilibria (716).
- carbon tetrachloride-iodine, surface tension of the system (717).
- ethyl acetate-cyclohexane azeotrope, effects of temperature and pressure on the composition (718).
- methyl alcohol-acetone ternary system, refractive indices and bubble points (705).
- methyl alcohol-acetone ternary system, vapor-liquid equilibria (605).
- toluene-cyclohexane, heats of mixing (711).
- water-acetone, surface tensions of the system (719).
 - ammonium fluoride (720).
 - benzophenone (721).
 - carbon dioxide at high pressures (722).
 - ethyl ether (723).
 - ethylene dichloride (723).
 - glycerol, relation of composition to density and surface tension of the system (724).
 - heptadecanol, liquid-liquid equilibria for the system (725).
 - hydrogen halides (726).
 - isoamyl alcohol, analysis of the three-component system (727).
 - methyl alcohol mixtures, application of the Piazza distillation apparatus to fractionation (728).
 - methyl alcohol, rectification in a continuous column (729, 730).
 - methyl alcohol, surface tension of the system (719).
 - methyl alcohol, vapor-liquid equilibria data of the system (731).
 - n*-propyl alcohol, vapor-liquid equilibria of the system (606).
 - triphenylcarbinol (721).

3-Heptanol as a solvent for extraction of ethyl alcohol from aqueous solutions (732).

Proof, Percentage and Specific Gravity

Table XXII

PROOF, VOLUME %, WEIGHT % AND SPECIFIC GRAVITY OF ETHYL ALCOHOL-WATER MIXTURES (733)

U.S. Proof degrees at 60°F	Volume % Ethyl Alcohol	Weight % Ethyl Alcohol	Volume % Water	Specific Gravity at 60°/60°F
0	0.0	0.00	100.00	1.0000
1	0.5	0.39	99.53	0.9993
2	1.0	0.80	99.06	85
3	1.5	1.19	98.58	78
4	2.0	1.59	98.12	70
5	2.5	1.99	97.65	63
6	3.0	2.39	97.18	56
7	3.5	2.79	96.71	49
8	4.0	3.19	96.24	42
9	4.5	3.60	95.78	35
10	5.0	4.00	95.31	28
11	5.5	4.40	94.85	21
12	6.0	4.80	94.39	15
13	6.5	5.21	93.93	08
14	7.0	5.61	93.46	02
15	7.5	6.02	93.01	.9896
16	8.0	6.42	92.55	90
17	8.5	6.83	92.09	84
18	9.0	7.23	91.63	78
19	9.5	7.64	91.18	72
20	10.0	8.05	90.72	66
21	10.5	8.45	90.27	60
22	11.0	8.86	89.81	54
23	11.5	9.27	89.36	49
24	12.0	9.68	88.90	43
25	12.5	10.09	88.45	37
26	13.0	10.50	88.00	32
27	13.5	10.91	87.55	26
28	14.0	11.32	87.10	21
29	14.5	11.73	86.65	16
30	15.0	12.14	86.20	10
31	15.5	12.55	85.75	05
32	16.0	12.96	85.30	00
33	16.5	13.37	84.85	.9794
34	17.0	13.79	84.40	89
35	17.5	14.20	83.95	84
36	18.0	14.61	83.50	79
37	18.5	15.03	83.06	74
38	19.0	15.44	82.61	69
39	19.5	15.85	82.16	64

Table XXII (continued)

**PROOF, VOLUME %, WEIGHT % AND SPECIFIC GRAVITY
OF ETHYL ALCOHOL-WATER MIXTURES**

U.S. Proof degrees at 60°F	Volume % Ethyl Alcohol	Weight % Ethyl Alcohol	Volume % Water	Specific Gravity at 60°/60°F
40	20.0	16.27	81.72	59
41	20.5	16.68	81.27	54
42	21.0	17.10	80.82	49
43	21.5	17.52	80.38	44
44	22.0	17.93	79.93	39
45	22.5	18.35	79.48	34
46	23.0	18.77	79.03	29
47	23.5	19.19	78.58	24
48	24.0	19.60	78.14	19
49	24.5	20.02	77.69	13
50	25.0	20.44	77.24	0.9708
51	25.5	20.86	76.79	03
52	26.0	21.28	76.34	.9697
53	26.5	21.71	75.89	92
54	27.0	22.13	75.44	87
55	27.5	22.55	74.98	81
56	28.0	22.97	74.53	76
57	28.5	23.40	74.08	70
58	29.0	23.82	73.62	64
59	29.5	24.24	73.17	59
60	30.0	24.67	72.72	53
61	30.5	25.10	72.26	47
62	31.0	25.52	71.81	41
63	31.5	25.95	71.35	35
64	32.0	26.38	70.89	29
65	32.5	26.81	70.43	23
66	33.0	27.24	69.97	17
67	33.5	27.67	69.51	10
68	34.0	28.10	69.05	04
69	34.5	28.53	68.59	.9597
70	35.0	28.97	68.12	90
71	35.5	29.41	67.66	84
72	36.0	29.84	67.19	77
73	36.5	30.28	66.72	70
74	37.0	30.72	66.25	62
75	37.5	31.16	65.78	55
76	38.0	31.60	65.31	48
77	38.5	32.04	64.84	40
78	39.0	32.48	64.37	33
79	39.5	32.92	63.90	25

Table XXII (continued)

**PROOF, VOLUME %, WEIGHT % AND SPECIFIC GRAVITY
OF ETHYL ALCOHOL-WATER MIXTURES**

U.S. Proof degrees at 60°F	Volume % Ethyl Alcohol	Weight % Ethyl Alcohol	Volume % Water	Specific Gravity at 60°/60°F
80	40.0	33.36	63.42	17
81	40.5	33.81	62.95	09
82	41.0	34.25	62.47	01
83	41.5	34.70	61.99	.9493
84	42.0	35.15	61.52	85
85	42.5	35.60	61.04	77
86	43.0	36.05	60.56	69
87	43.5	36.50	60.08	60
88	44.0	36.96	59.59	52
89	44.5	37.41	59.11	43
90	45.0	37.86	58.63	34
91	45.5	38.32	58.14	26
92	46.0	38.78	57.66	17
93	46.5	39.24	57.17	08
94	47.0	39.70	56.68	.9399
95	47.5	40.16	56.19	89
96	48.0	40.62	55.70	80
97	48.5	41.09	55.21	71
98	49.0	41.55	54.72	61
99	49.5	42.02	54.22	52
100	50.0	42.49	53.73	0.9342
101	50.5	42.96	53.24	32
102	51.0	43.43	52.74	22
103	51.5	43.90	52.25	12
104	52.0	44.37	51.75	02
105	52.5	44.85	51.25	.9292
106	53.0	45.33	50.75	82
107	53.5	45.80	50.26	72
108	54.0	46.28	49.76	62
109	54.5	46.76	49.26	52
110	55.0	47.24	48.76	41
111	55.5	47.73	48.25	31
112	56.0	48.21	47.75	20
113	56.5	48.70	47.25	10
114	57.0	49.19	46.75	.9199
115	57.5	49.68	46.24	88
116	58.0	50.17	45.74	77
117	58.5	50.66	45.23	67
118	59.0	51.15	44.72	56
119	59.5	51.65	44.22	44

Table XXII (continued)

**PROOF, VOLUME %, WEIGHT % AND SPECIFIC GRAVITY
OF ETHYL ALCOHOL-WATER MIXTURES**

U.S. Proof degrees at 60°F	Volume % Ethyl Alcohol	Weight % Ethyl Alcohol	Volume % Water	Specific Gravity at 60°/60°F
120	60.0	52.15	43.71	33
121	60.5	52.65	43.20	22
122	61.0	53.15	42.69	11
123	61.5	53.65	42.18	00
124	62.0	54.15	41.67	.9088
125	62.5	54.66	41.16	77
126	63.0	55.16	40.65	65
127	63.5	55.67	40.14	54
128	64.0	56.18	39.62	42
129	64.5	56.70	39.11	31
130	65.0	57.21	38.60	19
131	65.5	57.72	38.08	07
132	66.0	58.24	37.57	.8996
133	66.5	58.76	37.05	84
134	67.0	59.28	36.54	72
135	67.5	59.80	36.02	60
136	68.0	60.32	35.50	48
137	68.5	60.85	34.99	36
138	69.0	61.38	34.47	23
139	69.5	61.91	33.95	11
140	70.0	62.44	33.43	.8899
141	70.5	62.98	32.91	86
142	71.0	63.51	32.38	74
143	71.5	64.05	31.86	61
144	72.0	64.59	31.34	49
145	72.5	65.13	30.82	36
146	73.0	65.67	30.29	23
147	73.5	66.22	29.76	10
148	74.0	66.77	29.24	.8797
149	74.5	67.32	28.71	84
150	75.0	67.87	28.19	0.8771
151	75.5	68.43	27.66	58
152	76.0	68.92	27.13	45
153	76.5	69.54	26.60	32
154	77.0	70.10	26.07	18
155	77.5	70.67	25.54	05
156	78.0	71.23	25.01	.8691
157	78.5	71.80	24.47	78
158	79.0	72.38	23.94	64
159	79.5	72.95	23.40	50

Table XXII (continued)
PROOF, VOLUME %, WEIGHT % AND SPECIFIC GRAVITY
OF ETHYL ALCOHOL-WATER MIXTURES

U.S. Proof degrees at 60°F	Volume % Ethyl Alcohol	Weight % Ethyl Alcohol	Volume % Water	Specific Gravity at 60°/60°F
160	80.0	73.53	22.87	36
161	80.5	74.11	22.33	23
162	81.0	74.69	21.80	08
163	81.5	75.27	21.26	.8594
164	82.0	75.86	20.72	80
165	82.5	76.45	20.18	66
166	83.0	77.04	19.64	52
167	83.5	77.64	19.10	37
168	84.0	78.23	18.55	22
169	84.5	78.84	18.01	08
170	85.0	79.44	17.46	.8493
171	85.5	80.05	16.92	78
172	86.0	80.62	16.37	63
173	86.5	81.28	15.82	47
174	87.0	81.90	15.27	32
175	87.5	82.52	14.72	16
176	88.0	83.14	14.16	01
177	88.5	83.78	13.61	.8385
178	89.0	84.41	13.05	69
179	89.5	85.05	12.49	53
180	90.0	85.69	11.93	36
181	90.5	86.34	11.37	20
182	91.0	86.99	10.80	03
183	91.5	87.65	10.24	.8286
184	92.0	88.31	9.67	69
185	92.5	88.98	9.09	51
186	93.0	89.65	8.52	33
187	93.5	90.34	7.94	15
188	94.0	91.02	7.36	.8196
189	94.5	91.72	6.77	78
190	95.0	92.42	6.18	58
191	95.5	93.14	5.59	39
192	96.0	93.85	4.99	18
193	96.5	94.58	4.39	.8098
194	97.0	95.32	3.78	77
195	97.5	96.07	3.17	56
196	98.0	96.82	2.55	33
197	98.5	97.60	1.93	10
198	99.0	98.38	1.29	.7987
199	99.5	99.19	0.65	62
200	100.0	100.00	0.00	37

Table XXII (continued)

PROOF, VOLUME %, WEIGHT % AND SPECIFIC GRAVITY OF ETHYL ALCOHOL-WATER MIXTURES

Note that at a given proof reading, the volume % alcohol and the volume % water do not add up to 100%. This is to compensate for the shrinkage in volume which occurs when these two liquids are mixed. The volume % ethyl alcohol is equal to the parts by volume of pure ethyl alcohol in 100 parts of solution.

HOW TO REDUCE PROOF

Problem: Starting with 75 gallons of 190 proof ethyl alcohol, how much water should be added to make it 170 proof?

In Table XXII we find that 170 proof alcohol consists of 85 volume % pure alcohol and 17.46 volume % water. The ratio of alcohol to water which we wish to obtain after dilution is therefore 85/17.46.

Table XXII also shows that 190 proof alcohol consists of 95 volume % pure alcohol and 6.18 volume % water. Each 100 gallons of 190 proof alcohol therefore contains 95 gallons of pure alcohol.

If we let x equal the gallons of water which must be present with each 95 gallons of pure alcohol in order for us to have 170 proof alcohol, we get the proportion:

$$\frac{85}{17.46} = \frac{95}{x}$$

Solving, we get:

$x = 19.5$ gallons of water which must be present in the 170 proof alcohol.

Since 100 gallons of 190 proof alcohol already contains 6.18 gallons of water,

$19.5 - 6.18 = 13.32$ gallons of water which must be added to 100 gallons of 190 proof alcohol to make it 170 proof

But we are starting with only 75 gallons of 190 proof alcohol, therefore,

$13.32 \times \frac{75}{100} = 9.99$ gallons of water which must be added to 75 gallons of 190 proof alcohol to make it 170 proof

Table XXIII
VOLUME AND WEIGHT CONVERSION SCALE FOR
ETHYL ALCOHOL-WATER SOLUTIONS (733)

% Alcohol By Volume at 60°F	% To Be Converted	% Alcohol By Weight	% Alcohol By Volume at 60°F	% To Be Converted	% Alcohol By Weight
1.257	1	0.795	58.844	51	43.428
2.510	2	1.593	59.852	52	44.374
3.758	3	2.392	60.854	53	45.326
5.002	4	3.194	61.850	54	46.283
6.243	5	3.998	62.837	55	47.245
7.479	6	4.804	63.820	56	48.214
8.712	7	5.612	64.798	57	49.187
9.943	8	6.422	65.768	58	50.167
11.169	9	7.234	66.732	59	51.154
12.393	10	8.047	67.690	60	52.147
13.613	11	8.862	68.641	61	53.146
14.832	12	9.679	69.586	62	54.152
16.047	13	10.497	70.523	63	55.165
17.259	14	11.317	71.455	64	56.184
18.469	15	12.138	72.380	65	57.208
19.676	16	12.961	73.299	66	58.241
20.880	17	13.786	74.211	67	59.279
22.081	18	14.612	75.117	68	60.325
23.278	19	15.440	76.016	69	61.379
24.472	20	16.269	76.909	70	62.441
25.662	21	17.100	77.794	71	63.511
26.849	22	17.933	78.672	72	64.588
28.032	23	18.768	79.544	73	65.674
29.210	24	19.604	80.410	74	66.768
30.388	25	20.443	81.269	75	67.870
31.555	26	21.285	82.121	76	68.982
32.719	27	22.127	82.967	77	70.102
33.879	28	22.973	83.805	78	71.234
35.033	29	23.820	84.636	79	72.375
36.181	30	24.670	85.459	80	73.526
37.323	31	25.524	86.275	81	74.686
38.459	32	26.382	87.083	82	75.858
39.590	33	27.242	87.885	83	77.039
40.716	34	28.104	88.678	84	78.233
41.832	35	28.971	89.464	85	79.441
42.944	36	29.842	90.240	86	80.662
44.050	37	30.717	91.008	87	81.897
45.149	38	31.596	91.766	88	83.144
46.242	39	32.478	92.517	89	84.408
47.328	40	33.364	93.254	90	85.689
48.407	41	34.254	93.982	91	86.989
49.480	42	35.150	94.700	92	88.310
50.545	43	36.050	95.407	93	89.652
51.605	44	36.955	96.103	94	91.025
52.658	45	37.865	96.787	95	92.423
53.705	46	38.778	97.459	96	93.851
54.746	47	39.697	98.117	97	95.315
55.780	48	40.622	98.759	98	96.820
56.808	49	41.551	99.386	99	98.381
57.830	50	42.487	100.000	100	100.000

How to Use Table XXIII

Problem 1: 3% alcohol by volume is equal to what % alcohol by weight?

Solution. Locate the number 3 in the center column and look to the right to find that 3% by volume equals 2.392% by weight.

Problem 2: 3% alcohol by weight is equal to what % alcohol by volume?

Solution. Locate the number 3 in the center column and look to the left to find that 3% by weight equals 3.758% by volume.

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